

## ABSTRACT

Title of Dissertation: NUTRIENT RETENTION BY RIPARIAN FORESTED BUFFERS IN WESTERN MARYLAND: DO THEY WORK AND ARE THEY WORTH IT?

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Riparian buffers are a best management practice (BMP) implemented to improve water quality. In 1997, Maryland established the Conservation Reserve Enhancement Program (CREP) to give landowners incentives to install riparian buffers that would help restore the Chesapeake Bay.

Although many studies support riparian buffers as a BMP, many have also reported a wide range of nutrient reductions. It is uncertain what factors control buffer function, yet they continue to be installed with high expectations. Water quality predictions become less accurate in hydrogeologically complex systems such as the Ridge and Valley (R&V) physiographic province. The purpose of this research was to assess the riparian buffer's nutrient removal function of dissolved nitrogen and phosphorus in the R&V to understand the hydrologic controls further.

Throughout western Maryland, we conducted two synoptic stream chemistry studies that contained forest buffers planted under CREP and a range of pre-existing natural forested riparian zones. We used a steady-state reach mass balance model to estimate lateral groundwater inputs and tested several nutrient models to describe the nutrients in groundwater discharge. We then aimed to understand if incentives given through CREP to landowners were adequate by performing a benefit-cost analysis (BCA) using three scenarios. We used the BCA results to estimate nutrient reduction costs using results from the Chesapeake Bay Watershed Model (CBWM) and our synoptic studies.

Streams along CREP sites did not show strong evidence of nutrient retention. However, those containing a mix of natural forests with planted buffers showed significant nutrient declines in both synoptic studies. Several models tested (i.e., The Nature Conservancy model, Gburek and Folmar (1999), our base model) inadequately described nutrient discharge; however, our actual flow model performed best. Our BCA results found newly planted forest buffers under CREP provide the greatest financial gains to landowners, but grass buffers are the most cost-effective practice based on CBWM's estimated nutrient reductions. Although, our research did not assess grass buffers, our synoptic studies showed little indication that newly planted forest buffers significantly reduce nutrients in the R&V, suggesting stream water quality greatly depends on the watershed's hydrogeomorphology that controls how major contributing sources filter through the landscape.

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by

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# Chapter 1: The big picture: an overview of riparian buffer function and effectiveness

## ***1.1 Introduction***

The degradation of surface and subsurface waters from excessive nutrient pollution, sediments, and other contaminants from agriculture is a global concern (Hickey and Doran 2004, Lammers and Bledsoe 2017). One popular method to reduce contaminants is implementing riparian buffers as a best management practice (BMP). Riparian buffers are planted or naturally vegetated (herbaceous or woody) riverine, or littoral areas that protect adjacent aquatic systems (e.g., lakes, rivers, and streams) from upland land uses (Parkyn 2004, Dufour et al. 2019). During the 1960s, land managers began planting riparian buffers as a conservation practice (Polyakov et al. 2005), and only in the last few decades has their ability to abate nutrients and sediment from agricultural fields become a popular research topic (Vidon et al. 2018, Hill 2019). In the 1980s and 1990s, the nutrient removal mechanisms within riparian buffers were not well understood, and their level of importance had little agreement among researchers (Hill 2019). Today, land managers, state and federal agencies, and conservationists rely on riparian buffers to improve water resources heavily affected by nutrients and other pollutants in agricultural and rural catchments (Bernhardt et al. 2005b, Mayer et al. 2007).

The dependence on riparian buffers is reflected through the establishment of programs, such as the Conservation Reserve Enhancement Program (CREP) and the Environmental Quality Incentive Program (EQIP) (USDA 2001). These voluntary



programs promote buffer plantings on environmentally sensitive land (usually agricultural fields) near streams or other approved water bodies for a contract period. In return, landowners receive annual payments and reimbursements for the buffer establishment (Maryland Department of Natural Resources 2019a, USDA 2020). In addition to nutrient removal, riparian buffers serve a multitude of other benefits such as improving stream channel integrity by reducing stream bank and channel erosion, providing wildlife habitat, protecting property from flooding, supporting aquatic ecosystems, and providing shade that maintains a narrow temperature range of stream water for temperature-sensitive species (Wenger 1999). However, among these benefits, the focus of this dissertation is understanding and evaluating their nutrient removal efficacy because it is the least understood yet are expected to restore degraded waters where they are implemented. Riparian buffers are implemented as a best management practice to restore the water quality of surface waters impacted by nutrient pollution from agricultural practices, such as the Chesapeake Bay (US EPA 2018). Each established buffer theoretically reduces a certain amount of nitrogen (N), phosphorus (P), and sediment pollution from reaching adjacent waterways and researchers and land managers estimate the nutrient and sediment reduction using empirical models to measure progress towards achieving Total Maximum Daily Loads (TMDLs) (Jiang et al. 2020).

Although many studies support riparian buffer use in improving water quality, there are still areas of uncertainty. The mechanisms involved in riparian buffers that remove and attenuate nutrients and sediments are well understood, but less understood are the landscape conditions and buffer designs that are most critical to their function. Over the last few decades, researchers published numerous literature reviews and meta-

analyses on riparian buffers. Some have focused on the retention of a specific nutrient or sediment (Korom 1992, Mayer et al. 2007, Hoffmann et al. 2009, Yuan et al. 2009, Hill 2019), while others have investigated the characteristics of the riparian buffer (Wenger 1999, Lee et al. 2004, Sweeney and Newbold 2014) or the physical properties of the riparian area (Bendix and Hupp 2000, Steiger et al. 2005). Others have taken a more holistic approach in providing a succinct synthesis of all available data concerning riparian buffers (Norris 1993, Hickey and Doran 2004). The array of topics and conclusions presented in these reviews demonstrate the complexity of riparian buffer systems and how various factors may affect their functionality.

Studies performed in the Chesapeake Bay watershed shows nutrient removal varies spatially and temporally, especially when comparing the percent of nutrient retention among the physiographic provinces: Coastal Plain, Piedmont, Ridge & Valley (R&V), and Appalachian Plateau (Lowrance et al. 1997). Only a few studies have been performed in the latter two provinces, but current research shows highest retention of nitrate in the Coastal Plain (67 – 95%) compared to the other provinces (35 – 60% in the Piedmont & 25 – 50% in the R&V/Appalachian Plateau) (Lowrance et al. 1997, Weller et al. 2011). Therefore, the purpose of this chapter is to summarize published results and provide a thorough overview of riparian buffer function by: (1) defining the mechanisms that are responsible for nutrient and sediment retention within riparian buffers; (2) summarizing the range of nutrient and sediment reductions and the significant factors contributing to the variability of their success; (3) investigating the different methodology employed to estimate these reductions and how this may influence assumptions; and (4) discussing how riparian buffer function may change based on geographical locations and

landscapes. A thorough literature review examining these aspects in studies conducted throughout the world may provide better insight of the large variation of nutrient retention found throughout the Chesapeake Bay watershed and determine what scientific research is still needed to further improve our understanding of riparian buffer function.

## ***1.2 Nutrient and sediment reduction mechanisms***

### **1.2.1 Importance of the riparian area**

Ecologically speaking, riparian areas are active hydrological systems positioned in the low-lying areas of a landscape that connect uplands to waterways through a hydrological network. Surface and subsurface waters flow through the catchment and collect nutrients (N & P) and sediments along the way before discharging into an aquatic system (Dufour et al. 2019). The riparian area has the potential to intercept these constituents with dynamic microbial communities, biological diversity, and ecological complexity (Merill and Tonjes 2014) acting as a “zone of influence” (National Research Council 2002). Runoff and groundwater filtering through the riparian area undergo chemical transformations dependent on the riparian ecosystem's health and conditions (Merill and Tonjes 2014). In the interface between land and water, known as the hyporheic zone, groundwater and channel waters (e.g., streams) connect and exchange water and nutrients through bidirectional flows (Triska et al. 1993, Merrill and Tonjes 2014). These flows allow for chemical changes that can further affect stream water quality (Hedin et al. 1998, Baker et al. 2006, Merrill and Tonjes 2014). In the general riparian region, the biological and chemical mechanisms that retain nutrients and sediments depend on the flowpath through which it travels (i.e., subsurface or surface runoff) and whether the nutrient is soluble or sediment-bound (Tolkkinen et al. 2020).

### **1.2.2 Retention of nutrients in groundwaters**

In subsurface flows, soluble forms of N can be reduced via vegetation uptake, microbial uptake, and denitrification (Lowrance et al. 1997, Hickey and Doran 2004, Mayer et al. 2007). Vegetation can use many forms of soluble N, such as ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and dissolved organic nitrogen (DON) (Hill 2019); however, vegetation uptake only temporarily stores N. Once N is taken up by plant roots, it is quickly converted to organic nitrogen compounds and allocated to different parts of the plant (i.e., leaves, stems, or roots). Storage in branches and bark tissue increases in the summer and further amplifies once leaves begin to senesce. Although dependent on the tree species, generally, small trees contain 50% of total nitrogen within their leaves, where 75–80% is retranslocated back into the stem before fall leaf abscission (Tyrrell and Ralph J Boerner 1987, Dickson 1989). Nitrogen continues to accumulate into the stems and roots of trees late into the fall season (Tromp 1983, Kato 1986). Woody vegetation can store nitrogen for a long time, however, once vegetation dies or senesces, the plant material decomposes, and N is mineralized and leached back into the soil (Hickey and Doran 2004, Hill 2019). Vegetation removal is a permanent solution to removing nutrients from the ecosystem; however, a complete removal of the tree removes the carbon source necessary for denitrification (Hickey and Doran 2004). Soil disturbance can also increase erosion and elevate soil  $\text{NO}_3\text{-N}$  levels from mineralization from detritus (Lovett et al. 2005), leading to higher rates of leaching (Palmer et al. 2014).

Similarly, microbes can take up N and use it in their biomass that immobilizes it, but this also is not permanent. Microbes are also responsible for N mineralization and nitrification, where  $\text{NH}_4^+$  or  $\text{NO}_3^-$  may be produced depending on certain conditions (Jacinthe et al. 1998). Soil organic N can be quickly mineralized to  $\text{NH}_4^+$  in oxic or

anoxic conditions, but nitrification can only occur in oxic soils (water-filled pore space (WFPS) <80%) (Lupon et al. 2017). Microbial N uptake transferred to soil organic matter (SOM) has a greater potential of creating a long-term sink (Curtis et al. 2011), but this depends on the C/N ratio, where a lower ratio has less nitrate retention. Young forests generally have high C/N ratios than old growth forests, which is possibly a consequence of greater nutrient uptake to support rapid biomass accumulation, which decreases available N in the soil. Nonetheless, N sinks through SOM have not been found to be correlated with forest age (Fuss et al. 2019), and much uncertainty remains on what factors control whether SOM provides a long- or short-term sink (Lovett et al. 2018). Based on current data, denitrification is the only process that has strong evidence of permanently mitigating N by transforming it into a nearly inert gas (dinitrogen (N<sub>2</sub>)) (Korom 1992). When NO<sub>3</sub><sup>-</sup> enters an anaerobic environment (WFPS > 60%) (Linn and Doran 1984), bacteria use it as an electron acceptor in their metabolic process, where NO<sub>3</sub><sup>-</sup> is then reduced to N<sub>2</sub>, or less often, nitrous oxide (N<sub>2</sub>O) or nitric oxide (NO) (Korom 1992, Hickey and Doran 2004). Denitrification is considered the primary mechanism in removing NO<sub>3</sub><sup>-</sup> (Parkyn 2004) — the dominant form of N found in waterways draining croplands (Hefting et al. 2005).

Similar to N, vegetation and microbial uptake can temporarily remove dissolved forms of P (i.e., orthophosphate (PO<sub>4</sub><sup>3-</sup>), inorganic polyphosphates (polyP), and organic P compounds) (McDowell and Sharpley 2001, Abu-Zreig et al. 2003) in subsurface waters (Richardson and Marshall 1986, Hoffmann et al. 2009). The central and more long-term mechanisms are P sorption and precipitation (Richardson 1985, Richardson and Marshall 1986, Reddy et al. 1995, Hoffmann et al. 2009). P can adsorb onto clay minerals (Parfitt

1979, Domagalski and Johnson 2011), iron and aluminum oxides in acidic soils, or precipitate as calcium phosphate in alkaline soils (Litaor et al. 2003, Giesler et al. 2005, Hoffmann et al. 2009). Aluminum and iron oxides are considered the essential sequesters of P (Zhang and Huang 2007, Domagalski and Johnson 2011).

### **1.2.3 Retention of nutrients and sediment in surface runoff**

Surface runoff usually contains both soluble and sediment-bound N and P.

Sediment-bound nutrients and sediment can be retained in riparian areas when the water velocity is reduced, which subsequently increases infiltration into the soil profile and allows suspended matter to be sedimented out. Other than sediment itself, sediment trapping is more critical for mitigating P than N (less than 10–20% of total N in streams comes from sediment) (Vought et al. 1994). The primary form from cropland runoff is usually in particulate form (70–94%) (Sharpley and Smith 1989, Abu-Zreig et al. 2003). Large amounts of P from fertilizers and manure adsorb to soil particles and organic matter that are among the primary surface runoff pollutants (Hickey and Doran 2004). The deposition of sediment and the infiltration of surface runoff allows P and N to be adsorbed in the soil, which many studies have concluded are the principal mechanisms preventing P from reaching adjacent aquatic systems (Srivastava et al. 1996, Patty et al. 1997, Abu-Zreig et al. 2003).

### ***1.3 Factors influencing riparian buffer efficiency***

Although riparian buffers can effectively reduce N, P, and sediment from discharging into adjacent aquatic systems, many factors can affect their removal rates. The most studied factors are the riparian area's physical and chemical properties (e.g., hydrogeomorphological characteristics, soil properties, organic carbon availability) and

the buffer's characteristics (e.g., vegetation type, age, width). Researchers have found no consensus on which factors are the most influential; results obtained from some studies are contradicted by others. It is also challenging to determine how each individual factor affects riparian buffer function due to their interconnectedness and interdependencies. Nevertheless, the following sections discuss the essential research findings for these factors and characteristics.

### **1.3.1 Physical and chemical properties of the riparian area**

#### *Hydrogeomorphological characteristics*

Many of the nutrient and sediment retention mechanisms in riparian buffers fundamentally depend on hydrogeomorphological characteristics (i.e., interactions of surface and subsurface waters with the landscape) (Sidle and Onda 2004). A key factor controlling water infiltration is topographic slope. Steep slopes do not allow water to pond on the land surface, thus reducing infiltration, sedimentation, and nutrient retention (Dillaha et al. 1988, Liu et al. 2008, Hoffmann et al. 2009). A lesser topographic slope reduces overland flow velocities, allowing for greater rates of infiltration (Wenger 1999). Shallow subsurface flow through the riparian rhizosphere is also necessary for nutrient uptake by vegetation and microbes, adsorbance, and denitrification (Hawes and Smith 2005, Wohlfart et al. 2012, O'Toole et al. 2018), where riparian buffers with an aquitard less than 3 m deep have shown the highest efficiencies in nutrient retention (Devito et al. 2000). Older groundwaters (e.g., > 40 years) traversing through more extended, deeper flow paths may become anoxic (Böhlke and Denver 1995, Merrill and Tonjes 2014), thus providing conditions suitable for denitrification as well (Böhlke et al. 2007).

### *Soil texture*

The hydrological pathways in a riparian buffer that control nutrient and sediment retention also depend on soil texture. Soil texture is based on the relative percentage of clay, silt, and sand, which also affects soil porosity and permeability (Coyne and Thompson 2006, O'Toole et al. 2018). Soils high in clay have lower permeability which reduces the rate of subsurface flow through a riparian area's root zone; however, lower soil permeability can also generate more runoff during large, intense rainstorm events (Hawes and Smith 2005). Sandy soils have a larger grain size and higher soil permeability that enables higher infiltration and reduced overland runoff, although the more rapid transmission of water may lessen the opportunities for nutrient retention and abatement (Burt et al. 1999, Angier et al. 2005, Böhlke et al. 2007).

Studies investigating soil texture effects alone on nutrient and sediment reduction found it has little influence on N in surface and subsurface waters (Balestrini et al. 2016, Valkama et al. 2019), but considerable control over P and sediment (Dillaha et al. 1989, Lee et al. 1989). P retention is lowest where there is high clay content. In surface runoff, clay can bind to many sediment-bound nutrients, such as P, but it is less effectively removed by sedimentation. The fine particle size of clay is much more difficult to trap on land than larger, coarse materials (Hoffmann et al. 2009). In riparian regions with higher clay content, the low permeability reduces infiltration of surface runoff that can lead to direct flows to a stream. A wide buffer width with dense vegetation can provide the most optimal conditions by slowing surface runoff and allowing more time for infiltration to occur (Hoffmann et al. 2009).



### *Soil Geochemistry*

Sorption (attachment) properties of soil are most critical to long-term P retention and depend on the availability of iron (Fe) and aluminum (Al) oxides and precipitating agents; presence of competitors; and redox potential (Hoffmann et al. 2009). Fe(III) hydroxides that adsorb P can undergo reductive dissolution in anaerobic conditions, resulting in re-mobilization of Fe(II) and P (Patrick and Khalid 1974, Pant and Reddy 2001). While some studies have shown anaerobic conditions release P from the soil (Sallade and Sims 1997, Scalenghe et al. 2002), others have shown very little correlation between redox potential and P release (Khalid et al. 1977, Vadas and Sims 1998). In acidic and flooded conditions, iron and P will bind to form precipitates and minerals such as strengite (Jones 2020). In the event P is released, it may again be retained in the soil by non-reduced Fe(III) oxides or redox-stable components (Al oxides, calcite, and phyllosilicate clay), depending on availability (Darke and Walbridge 2000, Murray and Hesterberg 2006, Bechtold et al. 2017). Alternatively, in alkaline soil, P can precipitate as calcium phosphate or Fe(II) phosphate (Moore and Reddy 1994, Shenker et al. 2005, Hoffmann et al. 2009). P loss to aquatic systems is more likely to occur in P saturated soils (Hickey and Doran 2004) or where there is limited sorption capacity with too many competing ions (i.e., hydrogen ion, magnesium, and sulfate) (Nriagu 1972, Lamers et al. 1998, Smolders et al. 2001, Domagalski and Johnson 2011). Furthermore, a recent study found that the decline in atmospheric N deposition over the last 20 years is reducing  $\text{NO}_3^-$  concentrations in the soil, making  $\text{NO}_3^-$  less available as an electron acceptor in redox reactions. Consequently, more Fe(III) is being reduced, further limiting P sorption capacity, but this was less observed in catchments dominated by agriculture that continue

to receive large N inputs from fertilizer (Musolff et al. 2017). Although iron is the fourth most common element in the earth's crust, environmental factors can affect its chemical forms and thus its availability. Environments most conducive to the conversion of Fe(III) to Fe(II) through microbial activity is soils saturated in Fe(III), contain low pH (<4.5), and are anaerobic or commonly flooded. Once iron is in ferrous form (Fe(II)), it is also more readily available to plants (Jones 2020).

### *Soil carbon*

Carbon is considered an essential component for denitrification reactions (Merill and Tonjes 2014), bacterial growth and heterotrophic nitrification (albeit a process more commonly performed by chemoautotrophs) (Triska et al. 1993), and P and N absorption (Cahn et al. 1992, Reddy et al. 1998). Many studies emphasize the importance of carbon in topsoil but buried carbon layers may be of greater importance for denitrification. Carbon-rich soils are considered hotspots and can range from the topsoil to depths up to several meters (Hill et al. 2004, Kellogg et al. 2005, Blazejewski et al. 2009). Soil organic carbon also can increase P and N sorption in soils (Reddy et al. 1998) by creating humic-Fe(Al) complexes (Gerke and Hermann 1992). However, once organic carbon is reduced to dissolved organic carbon (DOC), the increase in DOC can become a more critical P mobilization mechanism than the reduction of Fe(III) (Hutchison and Hesterberg 2004). DOC comprises organic acids from plant roots, microbes, and fulvic-humic compounds (Swift 1996) that compete with P for surface binding sites (Violante et al. 1991, Bolan et al. 1994).

### **1.3.2 Characteristics of the buffer**

#### *Vegetation type*

The effect vegetation type (i.e., forest or herbaceous) has on nutrient and sediment retention is a common research topic with varying conclusions in current research.

Herbaceous buffers are relatively effective in reducing particulate N and P and sediment pollution because they create hydraulic roughness that slows surface runoff velocity, thus facilitating higher infiltration and sediment trapping (Mekonnen et al. 2016, Cole et al. 2020). Grasses can quickly form dense communities and survive throughout the year (Dosskey et al. 2010, Cole et al. 2020), enabling them to reduce sediment and pollutants soon after implementation with little seasonal effect (Lin et al. 2011, Erktan et al. 2013). Stiff-stemmed species, such as switchgrass and fescue, are most effective at reducing flowrates (Liu et al. 2008, Yuan et al. 2009) and are less likely to be damaged during heavy storm events (Yuan et al. 2009). However, during smaller rain events, stiff grasses are less effective (Dabney et al. 1993, Ritchie et al. 1997, Blanco-Canqui et al. 2004b, 2006). Generally, in management settings, one or two species are planted (Erktan et al. 2013, Valkama et al. 2019), but higher species diversity is more effective at retaining sediment and more resilient to environmental stressors (e.g., extreme temperatures and flooding) (Cole et al. 2020).

Riparian forest buffers usually consist of multiple species and may be as effective as herbaceous buffers in decreasing surface flow velocity, depending on their structural complexity (e.g., ground vegetation, stem density, leaf litter, and fallen deadwood) (Zhang et al. 2010, Cole et al. 2020). A forest buffer's root system complexity and depth can influence soil permeability, infiltration rates, water retention, and stabilization of sediments (O'Hare et al. 2016, Perez et al. 2017, Cole et al. 2020). Forest buffers are also

found to be more effective at removing sediment-bound and dissolved P (Kelly et al. 2007, Sjøvik and Syversen 2008) by promoting water infiltration and residence time that can affect sedimentation and sorption (He and Walling 1997, Kronvang et al. 2007). Woody vegetation P uptake rates are higher than herbaceous species because of larger mycorrhizal and root surface areas (Kelly et al. 2007). However, dense herbaceous vegetation can trap more coarse sediment and sediment-bound nutrients (Yuan et al. 2009). Although sediment trapping is important to improve surface water quality in general (Basnyat et al. 1999), coarse sediment trappings, such as sand, have little effect on P reduction because it has little nutrient holding capacity (Weaver and Summers 2014).

Despite these findings, other studies found no differences between the two vegetation types (Schmitt et al. 1999, Lowrance and Sheridan 2005, Syversen 2005) and some found forest buffers may release P. Typically, forest buffers provide more organic matter containing particulate P that can remobilize into a soluble form when microbes detect low availability of soluble P. However, microbes may remobilize P before it is needed, where it will then reenter surface and subsurface waters (Roberts et al. 2012). Furthermore, the macropores created by forest buffer root systems may create a quick getaway for colloidal P, further reducing P retention (Kelly et al. 2007).

Both grass and forest buffers were found inadequate at removing soluble N in surface waters (Barling et al. 1994, Mayer et al. 2005, Valkama et al. 2019), but many studies conclude forest buffers are more effective at removing  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in subsurface waters (Osborne and Kovacic 1993, Mayer et al. 2005, Valkama et al. 2019), where most N transformations occur (Peterjohn and Correll 1984, Mayer et al. 2005).

However, some studies found no significant differences between vegetation types at removing insoluble N (Wenger 1999, Mayer et al. 2007, Valkama et al. 2019). Those that did find a difference attribute the most effective removal rates from plant uptake (Fennessy and Cronk 1997, Martin et al. 1999b), although the primary mechanism of  $\text{NO}_3^-$  removal is denitrification (Addy et al. 1999, Parkyn 2004). Vegetation can obtain N from several sources (e.g., mineralization of soil organic matter, atmospheric N inputs, and contaminated sediments) (Hill 2019). A study using isotopes to quantify the amount of  $\text{NO}_3^-$  removed via denitrification and vegetation uptake found denitrification was responsible for 75% of  $\text{NO}_3^-$  removal in autumn (Dhondt et al. 2003), and other studies have found  $\text{NO}_3^-$  removal is highest in the winter when vegetation uptake is minimal (Haycock and Pinay 1993, Hickey and Doran 2004). The seasonal fluctuation of groundwater levels may also limit when plant roots have access to groundwater (Hill 2019) that may cause plants to seek other sources.

Overall, there is no clear evidence that vegetation uptake is an effective mechanism for  $\text{NO}_3^-$  removal in groundwater. Contradictory conclusions from many studies make it difficult to discern clear management strategies, and likely, other interconnected factors within buffers dictate uptake rates. Indirect influences of vegetation may be more critical (Hill 2019), as their physiology and structure can affect nutrient and sediment reduction in multiple ways (Cole et al. 2020). A possible explanation of the observed differences between the vegetation types is that forest soils provide environments more conducive to denitrification and other microbial processes by supplying mineralizable sources of organic carbon from leaf litter, root decay, and root

exudates (Cooper 1990, Haycock and Pinay 1993, Broadmeadow and Nisbet 2004, Parkyn 2004).

### *Buffer age*

The age of buffer vegetation affects nutrient retention in some capacity, but it is unclear if mature or younger vegetation is more efficient. Some studies have found that younger forests and shrubs take up more nutrients than mature buffers because they are in the active growth phase and have high microbial activity and adsorption capacity in soils (Haycock et al. 1993, Mander et al. 1997, Broadmeadow and Nisbet 2004, Parkyn 2004). Contrarily, other studies have found that buffers become more effective with age (Peterjohn and Correll 1984, Lowrance et al. 1997, Addy et al. 1999, Mayer et al. 2007, Orzetti et al. 2010). For instance, Orzetti et al. (2010) found that  $\text{NO}_3^-$  reduction and stream habitat were positively correlated with buffer age and found significant differences between what they categorized as "younger" (buffers established less than ten years) and "older" (buffers established over ten years ago). Newbold et al. (2010) and Groh (2018) also found significant increases in  $\text{NO}_3^-$  reduction a decade after the buffer was established (Hill 2019). Root depth, density, and biomass and organic matter are expected to increase over time, resulting in more favorable denitrification conditions with higher carbon concentrations (Lammers and Bledsoe 2017). However, according to a meta-analysis performed by Valkama et al. (2019), buffer age does not affect  $\text{NO}_3^-$  retention in groundwater. Furthermore, in surface runoff, they found  $\text{NO}_3^-$  and total N increased in older buffers, indicating they were sources.

Greater root depth of mature vegetation can also increase accessibility to deeper groundwaters (Gurwick 2007, Hill 2019). About 96% of the root biomass of an 80-year-

old red maple (*Acer rubrum* L.) was found in the upper 30 cm of a 0–100 cm soil core (Gurwick 2007). Another study measured the upper 20 cm of soil in a riparian woodlot and found 60% of the root biomass of a 54-year-old buffer containing sugar maple (*Acer saccharum*), 74% of a 73-year-old white cedar buffer, and 99% of a 200-year-old eastern hemlock (*Tsuga canadensis*) (Fortier et al. 2013). However, in Sánchez-Pérez et al. (2008), very few roots were observed 60 cm below the soil surface in a riparian hardwood forest. In comparison to water table depth, Hill (2018) found that for at least five months of the growing season, 60% of study sites had water table depths >50 cm, and more than 30% were >100 cm (Hill 2019). These changes in the water table depth can limit nutrient retention via plant uptake.

Old and mature riparian forests improve sediment and particulate N & P retention by supplying sizeable woody debris along the forest floor, increasing hydraulic roughness and subsequent infiltration (Montgomery 1997, Broadmeadow and Nisbet 2004). In older herbaceous riparian buffers, the retention capacity of dissolved P was shown to increase with a higher percentage of vegetation cover (Schmitt et al. 1999, Abu-Zreig et al. 2003). In another study, sediment pollution was significantly reduced ten years after implementing a riparian buffer. The authors, however, attributed this to improved bank and channel stability after putting fences up to keep livestock out of the stream. Furthermore, the data revealed a reduction in TN concentrations, while TP concentrations remained constant. The unchanged P concentrations may have been due to sandy soils and low Fe concentrations (McKergow et al. 2003).

### *Buffer width*

Many riparian buffer studies have focused on buffer width as a factor in nutrient reduction. Generally, the wider the buffer, the greater the nutrient and sediment retention (Mayer et al. 2007, Orzetti et al. 2010). Broadmeadow and Nisbet (2004) conducted a literature review to determine an adequate riparian forest buffer width. They observed that narrow buffers supported denitrification, while wider buffers were necessary for sediment retention. Although buffer width somewhat depends on a buffer's intended purpose, it may be necessary to adjust buffer width as a way of compensating for a particular catchment's physical feature (Hill et al. 2004).

Slope, vegetation type and density, and soil particle size are the main physical features that should be considered when determining optimal buffer width. Under lower topographic slopes, a dense and narrow vegetated buffer is likely efficient for sediment retention (Robinson et al. 1996, Lee et al. 1998, Blanco-Canqui et al. 2004a), while under steeper topography with less vegetation, a wider buffer may be recommended (Daniels and Gilliam 1996). In shallow slopes, a 10-m buffer is most efficient based on riparian buffers showing a substantial sediment retention rate up to the first 10 m, with minimal retention thereafter (Dorioz et al. 2006, Liu et al. 2008, Cole et al. 2020). Clay and soils with smaller particle sizes may require a wider buffer (Dosskey et al. 2008). Buffer width is commonly not a factor in N retention, however (Mayer et al. 2005, Zhang et al. 2010, Valkama et al. 2019). P retention is influenced by width but less so than sediment — possibly a response to P's absorption to smaller particles (Schmitt et al. 1999). However, P uptake does show more of a positive correlation with buffer width than sediment. In a 10- and 15-m buffer, 92% and 91% of sediment were removed, respectively, and 67%



and 79% of P were removed (Abu-Zreig et al. 2003). A 16-m-wide buffer with a high density of herbaceous and woody species was most effective in retaining P (Lee et al. 2000). Despite studies concluding no correlation between N and buffer width, theoretical models developed from a literature review of 74 studies calculated a 30-m buffer was efficient in removing more than 85% of both N and P (Zhang et al. 2010).

### **1.3.3 Research methods**

The interest in riparian buffer efficacy in mitigating nutrients and sediment has dramatically increased in the last few decades. A large part of this interest stems from researchers' interest in determining the most important explanatory variables influencing riparian buffer function. Researchers who have attempted meta-analyses and literature reviews find that differences in study interests (Dufour et al. 2019), method designs (Osborne and Kovacic 1993, Hoffmann et al. 2009, Lammers and Bledsoe 2017, Hill 2019), and the lack of reporting standard statistical results (e.g., means, sample sizes, and variances of controls) (Valkama et al. 2019) make it challenging to define the most prominent controls on buffer function.

Dufour et al. (2019) performed a literature review focusing on how the research on riparian buffers changed from 1949 to 2015. Riparian buffer research expands across biodiversity, forestry, water quality, hydromorphology, restoration, and ecology disciplines. Riparian zone definitions differed amongst researchers, as some defined it based on hydrological characteristics, while others' delineations relied on geomorphological and biological characteristics. The attraction to study buffers from a wide range of specializations could explain the complexity and uncertainty of identifying crucial factors that affect riparian buffer function.

In a literature review highlighting how hydrological and biochemical processes affect P retention efficacy in riparian buffers, Hoffmann et al. (2009) summarized results across nine studies to explain factors controlling total and dissolved P. Each of the studies reported slope, soil type, buffer width, and vegetation type as significant covariates that interact with the retention mechanisms of TP and dissolved P. The methods in each of these studies ranged from simulation experiments conducted over several days (Lee et al. 2000, Abu-Zreig et al. 2003) to measuring responses caused by natural rain events over ten years (Uusi-Kämpä 2005). Differences in timeframes and study designs may also complicate how results should be interpreted when making a direct comparison (Osborne and Kovacic 1993, Lammers and Bledsoe 2017). Nonetheless, one study that involved a simulation experiment utilizing artificial runoff, showed that the efficiency of P trapping from vegetative buffers was comparable to results from studies using natural rainfall (Abu-Zreig et al. 2003). Hoffman et al. (2009) developed theories using the commonly measured factors to explain P retention, but each study measured its own additional metrics to investigate their research sites further. The individual studies concluded significant explanatory variables that differed from Hoffmann et al. (2009). This difference in the authors' selection of the most critical variables highlights how less popular metrics that cannot be easily summarized or evaluated through an assemblage of publications may be missed.

Methods employed to understand a specific riparian buffer function (e.g.,  $\text{NO}_3^-$  retention) in particular landscapes also restrict what we know. Hill (2019) argues that ambiguity in the mechanisms controlling groundwater  $\text{NO}_3^-$  removal exists because most research has been done in commonly occurring landscapes (regions with coarse-textured

sediment on sloping areas with surficial sand aquifers) with little focus on more complex systems. More research is apparently needed in landscapes with weathered bedrock, glacial till, and karst geology. Standard field methods used in these landscapes to assess  $\text{NO}_3^-$  removal from groundwater quantify the percent removal efficiency rather than the quantity of  $\text{NO}_3^-$  removal. This fails to capture the large spatial and temporal variations in groundwater discharge and nitrate concentrations. This narrow focus can underestimate the magnitude of the riparian buffer's efficiency and not reveal any information about the responsible chemical and biological processes involved. Future studies should focus on interactions between the physical landscape (sediment, lithology, stratigraphy, carbon), hydrological pathways, and chemical compositions ( $\text{NO}_3^-$ , P, and DOC) to improve our knowledge of how these factors affect nutrient removal. Long-term riparian buffer restoration studies on the watershed scale that focus on these mechanisms can help determine specific relationships required for sustainable nutrient removal (Hill 2019).

Although the boundless approaches in studying the effects of riparian buffer function can create some caution when comparing results, meta-analyses and literature reviews are a practical approach to synthesize data to reveal patterns. However, there is a risk that critical data is not incorporated in meta-analyses when standard statistics are missing. Valkama et al. (2019) reported in their meta-analysis on N retention that many studies conducted outside of North America were not included because they neglected to report means, sample sizes, and variances.

#### ***1.4 Location — does it matter?***

Processes are known to vary spatially within riparian buffers, and thus, generalizing theories across different environments can be dangerous (Bendix and Stella

2013). The mechanisms responsible for nutrient removal in riparian buffers depend on several interrelated factors that are assumed to vary across geographic locations (e.g., climate) and landscapes (e.g., physiographic provinces). This next section is an overview of how these factors may affect riparian buffer function.

#### **1.4.1 Geographic location**

Climate has been shown to be a significant predictor of denitrification, with highest rates in temperate and continental climates where there are no dry seasons and summers are warm or hot (Lammers and Bledsoe 2017). However, the authors of the study admitted that these climates were the most represented, and only five climates were used in their analysis. They explain climate was estimated using latitude but did not mention the other defined climates represented in their study (Lammers and Bledsoe 2017).

A meta-analysis comparing N retention rates in surface and subsurface flows across several continents and climates found no significant results, except rates between surface and subsurface waters in North America and humid subtropical climates. The study incorporated articles from United States, Netherlands, Australia, Finland, United Kingdom, Italy, Canada, New Zealand, Kenya, and China. The climates were humid continental, humid subtropical, Mediterranean, and oceanic using Köppen climate classification (Valkama et al. 2019). However, reviews that focus on the Mediterranean (Lupon et al. 2017) and temperate climates (Martin et al. 1999a) indicate more variability. Mediterranean climates have ample amounts of organic N from leaf litter and wet conditions in spring and fall that result in high N mineralization and nitrification rates (Medici et al. 2010, Lupon et al. 2015), but reduced denitrification in dry summers

because the soils never became fully saturated (Bernal et al. 2007, Davis et al. 2011, Lupon et al. 2017). In temperate climates, riparian soils are more commonly saturated, and denitrification rates are higher (McClain et al. 2003, Vidon 2010). In comparison, microbial activity and denitrification rates in arid environments are limited by water availability, resulting in very little production and loss of N in the riparian zones (Harms and Grimm 2010, Dijkstra et al. 2012).

Data on P removal across multiple geographic locations that would allow any observable trends is lacking (Lammers and Bledsoe 2017). Studies that have examined seasonal variations have reported declines in P attenuation in colder climates, likely due to reduced vegetative cover and growth from freezing and thawing events (Hoffmann et al. 2009). We can infer those geographic locations with colder climates have less P attenuation than climates with longer warm, growing seasons from these studies. However, without conclusive information, we can only speculate.

#### **1.4.2 Geographic landscapes**

Riparian buffers can reduce 100% of  $\text{NO}_3^-$  from subsurface waters (Hill 1996, Dosskey 2001), but at some sites, very little  $\text{NO}_3^-$  is reduced (Correll 1997, Snyder et al. 1998). Many researchers have suggested that the hydrogeological characteristics of a catchment have a substantial influence on the nutrient removal capacity of riparian buffers, which can vary across different landscapes (Schnabel et al. 1994, Hill 1996, Lowrance et al. 1997, Baker et al. 2001).

In southern Ontario, Canada, researchers investigated the hydrogeologic characteristics of eight sites located on glacial till and outwash landscapes to determine how the landscape's characteristics influenced  $\text{NO}_3^-$  removal during high water table

conditions. The results highlighted the importance of the following physical characteristics of the riparian area: aquiclude depth, slope, and soil texture. Using these three characteristics, they developed several riparian hydrologic types and hypothesized riparian buffer capacity and effective buffer widths. Their hypothetical buffer capacity ranged from small to large  $\text{NO}_3^-$  sinks, with the majority predicted to be in the small to medium category, and buffer widths ranging from less than 20-m to 60-m. Some hydrologic types had no recommended widths, such as sites containing soils with high hydraulic conductivity with deep flowpaths greater than 6 m deep where groundwater is expected to bypass the riparian zone entirely (Hill et al. 2004).

Other hydrological pathways that occur in complex landscapes that can affect buffer function are seeps and springs. Groundwater seeps are common in non-glaciated Appalachian Ridge and Valley (R&V) regions (Williams et al. 2014), glacial outwash, and till areas of North America (Vidon and Hill 2004). They occur when groundwater reaches the surface and seeps out of the soil's macropores as springs that generate surface flow as a small stream or rivulets (Hill 2019). The presence of seeps has shown to be an indicator of a shallow water table and young groundwater discharge (Lindsey et al. 2003). Springs generally have higher flow rates and can discharge water 13 times faster than diffuse flow (Shabaga and Hill 2010). These high-flowing springs are usually in areas with steeper slopes that are inconducive to diffuse flow. Groundwater seeps and springs may require wider buffer widths for the waters to have time to infiltrate into the soil to facilitate nutrient removal processes (Vidon and Hill 2004).

Nutrients carried in springs depend on where the springs originated and their flowpath. Streams in the Catskill Mountains of New York, a glaciated region, contain

waters from shallow and deep groundwater flow from bedrock fractures that discharge as perennial springs. Shallow groundwater has more potential for  $\text{NO}_3^-$  removal. However, deep groundwater can maintain  $\text{NO}_3^-$  concentrations (Ranalli and Macalady 2010), such as the recently mentioned deep groundwater flowpaths that can bypass riparian buffers' root systems (Lowrance et al. 1997). Karst landscapes, found throughout the R&V, present a complex hydrological system comprised of losing streams, springs, and fractured bedrock (Gburek and Folmar 1999a, White 2002, Pronk et al. 2009, Husic et al. 2019) that may affect riparian forest function and the amount of time it takes before seeing water quality improvements.

The response from installing riparian buffer BMP's may depend on groundwater residence time. Catchments containing groundwater with short residence times typically see water quality improvement 1 to 5 years after implementation, but catchments with longer residence times may require at least 20 years (Lindsey et al. 2003). A study that estimated the age (residence time) of spring water from the Chesapeake Bay Watershed from four hydrogeomorphic regions found ages ranged from 0 to 60 years in the Coastal Plain Uplands, 2 to 30 years in Piedmont crystalline, 10 to 20 years in the R&V carbonate, and 0 to 50 years in the R&V siliciclastic. Ages across the hydrogeomorphic regions were not significantly different, but waters were younger under wet conditions and sampled wells were older than those collected from springs. Models created in this study found that most of the streams at these sites will not show any response to BMPs for at least a decade from the time of installation. This time frame depends on the water source distribution of the stream (i.e., groundwater discharge (young and old), runoff, and springs) (Lindsey et al. 2003). Boyer et al. (2005) investigated if water quality improved

11 years after several nutrient management practices were implemented in a karst region in West Virginia and found no significant evidence of water quality improvement.

Similarly, Sutton et al. (2010) studied the effects of riparian buffers in improving N and P concentrations in streams located in the Chesapeake Bay Watershed Coastal Plain and reported no improvement in water quality. Riparian buffers ranged from recently implemented to 8 years old.

### ***1.5 Conclusions***

As discussed above, there are several independent and interconnected factors that affect riparian buffer function. The degree of importance that these factors have on buffer function is uncertain due to natural variations and contradictions in almost every aspect.

The riparian area's hydrological characteristics have considerable control of how nutrients and sediment interact within the buffer. This is influenced by depth to a confining layer, the groundwater's residence time, soil texture, and slope. For surface waters, the most optimal hydrologic conditions are shallow aquitards about 3 m deep, soils with medium permeability and hydraulic conductivity, available soil organic carbon, and a moderate slope that allows water to flow across the riparian region and filter through the soil. Similar conditions are suitable for subsurface waters, provided there is longer residence time for plant uptake and microbial processes while creating conditions conducive to denitrification.

Vegetation type, age, and width of the riparian buffer lack consistent evidence that they are significant factors. Both herbaceous and forest buffers effectively remove sediment, P and N. Denitrification is the primary mechanism for  $\text{NO}_3^-$  removal and is supported by both vegetation types. Grass buffers efficiently slow surface runoff by



creating hydraulic roughness that subsequently facilitates infiltration and sediment trapping. Forest buffers typically have less ground cover (Osborne and Kovacic 1993, Cole et al. 2020) but can increase infiltration rates from their structural and root system complexity. Forest buffers have higher P uptake rates than herbaceous species, but herbaceous species can trap more coarse sediment and sediment-bound nutrients. Forest buffers may also remove more soluble N from subsurface waters due to higher plant uptake.

Riparian buffer age may affect nutrient retention, but results vary. Some studies show that younger vegetation is more efficient because they are in the active growth phase and have high microbial activity. Their soils are not saturated with nutrients, which provides plenty of adsorption sites. Other studies found mature riparian buffers are more beneficial because of their longer root depth, higher accumulation of organic matter, and greater groundcover complexity that increases hydraulic roughness. Management strategies that promote grass, and young and mature forest buffers together may be more beneficial. In 1991, the United States Department of Agriculture and other government and private agencies identified specific zones that should be included in riparian forest buffer systems that would incorporate permanent woody vegetation, an area of managed forest, and an herbaceous filter strip (Welsch 1991, Lowrance et al. 1997). Currently, CREP offers separate incentives for each conservation practice (CP): riparian forest buffers (CP 22) and herbaceous buffers (CP 21). In CP22, an herbaceous strip may be added to address erosion and runoff. However, there are no CP's promoting the installation of a riparian buffer that includes all the specified zones identified in the

riparian forest buffer system's earlier designs (Natural Resources Conservation Service 2012).

Buffer width is a significant factor, but how wide depends on the slope, vegetation type and density, particle size, geographic location, and the purpose for the buffer. Studies show width has a more significant influence on sediment and P retention than N; however, wider buffers will increase residence time, thus facilitating N removal. In management contexts, private property and active agricultural boundaries limit the available space to plant buffers and, therefore, the potential nutrient and sediment reduction.

More research is needed to understand the role of riparian buffers in abating nutrient and sediment pollution in agricultural landscapes, especially buffers located in areas that have been much less studied. One region includes the Ridge and Valley (R&V) physiographic province of the Appalachian Mountains region, where karst and spring geology can affect stream water quality beyond the riparian buffer's capacity, depending on its flowpath and discharge location. It is essential to ensure riparian buffers in this province are effective since the R&V province comprises 32% of the Chesapeake Bay watershed (Lowrance et al. 1997). Riparian buffers continue to be planted in the R&V with the expectation that these BMP's are effectively reducing nutrient and sediment pollution and thus helping to meet nutrient reduction goals of the Chesapeake Bay. It is possible that stream water quality may not show signs of improvement until a decade or more after a buffer has been installed. Conservation programs such as CREP have 10–15-year contract periods. Once a particular contract has expired, a landowner has the right to remove the buffer. Therefore, it is particularly crucial to assess how well these BMPs

mitigate water pollution during the 10–15-year period during which time they are under contract.

### ***1.6 Motivations and thesis structure***

The overarching goals of the research are to: (1) determine how well riparian forest buffers function within in the Ridge and Valley (R&V) physiographic province of the Chesapeake Bay watershed and (2) understand the primary drivers influencing the efficacy of nutrient (N and P) retention. Although there is a general lack of data supporting the success of riparian buffers in mountainous regions, they continue to be used as a BMP in major basins like the Potomac River watershed where agricultural fields comprise 75% of the area of the Great Valley Carbonate region. The Great Valley Carbonate is a subunit of the Great Valley subprovince of the R&V. It is underlain by limestone and dolomite bedrock with fertile soils and gently sloping terrain making it conducive to farming (Miller et al. 1997). Farms are usually located near streams in this province because farmers prefer to farm land at the lowest slopes with tillable soil, usually directly adjacent to streams. Therefore, there are many agricultural fields near streams in the Appalachian Provinces compared to the Piedmont and Coastal Plain, making it more critical that riparian buffers work optimally in the R&V (Baker et al. 2006).

The subsequent chapters of the dissertation are organized in the following manner. Chapter 2 is a regional-scale (i.e., county-wide) synoptic survey of streams during baseflow conditions to assess buffer efficiency along reaches throughout western Maryland. Chapter 3 complements Chapter 2 by investigating the same issue but narrows its focus on four representative R&V subwatersheds where buffers have been widely

implemented. Chapter 3 attempts to discern if riparian hydrologic pathways control forest buffer function by characterizing the primary water sources of the stream from headwaters to the final outlet using a synoptic stream chemistry survey under baseflow conditions. The data of this chapter was combined with data from chapter 2 to estimate an average reduction of total dissolved nitrogen (TDN) from riparian buffers implemented under the Conservation Reserve Enhancement Program (CREP) in the R&V. In Chapter 4, the estimated average reduction of TDN in Chapter 3 was used in a benefit-cost analysis to estimate the economic costs to remove TDN loads and evaluate the potential gains landowners receive who participate in CREP to determine if it is an effective government-sponsored program. Lastly, Chapter 5 is a summary of findings, remaining questions, and suggested future research.

## Chapter 2: Assessing nutrient removal function of mature and recently planted riparian forested buffers in the Ridge and Valley

### *2.1 Abstract*

Riparian forests are often considered a best management practice for reducing nutrients in ground- and surface- waters originating from upland agricultural fields. Few studies have been conducted in the Ridge and Valley (R&V) physiographic province of the Chesapeake Bay watershed where complex hydrological conditions have the potential to amplify the variation in the function of riparian forests and, on average, reduce their functionality. To investigate how hydrological factors affect riparian forest function, we conducted synoptic stream chemistry surveys under baseflow conditions across the R&V focusing on two groups of stream reaches (i.e., ‘randomly selected’ and ‘special interest’ sites). ‘Randomly selected’ sites contained natural, pre-existing riparian forests and ‘special interest’ sites contained young riparian forests planted under the Conservation Reserve Enhancement Program. The two groups allowed a comparison between the functionality of mature and young riparian forests on nutrient mitigation. Nutrient (N and P) concentrations and stream water discharge measurements were taken at upstream and downstream locations, an average of 360 meters apart, to estimate lateral groundwater inputs (and concentrations) using a steady-state reach mass balance model. Canopy cover and riparian areas within a 1.5 m of stream elevation were estimated using GIS analysis of Multi-Resolution Land Characteristics Consortium data. Overall, estimated N and P concentrations of lateral inputs negatively correlated with canopy cover and forested riparian regions in streams of ‘randomly selected’ sites more often than ‘special interest’

sites. This implies a stronger potential for mature riparian forests to intercept N and P than recently planted. We also found the flow discharge along a stream dictated the functionality of riparian forests. The Nature Conservancy and Gburek and Folmar (1999) models used to predict water quality conditions using catchment-based land use/land cover were found inadequate, further demonstrating the complexity of the landscape and lack of spatial transferability of nutrient models to the R&V. The reach mass balance approach implies that stream-groundwater exchange largely controls the biological processes that affect nutrient concentrations and loads, potentially more so than in-stream nutrient processing, under spring baseflow conditions.

## ***2.2 Introduction***

Large amounts of nitrogen (N) and phosphorus (P) within watersheds are linked to agricultural sources, including fertilizer and farm animal waste (Doney et al. 2009). Currently, these nutrients represent the largest contributor to water quality degradation across the Chesapeake Bay watershed (US EPA 2018). Reforested riparian buffers have been shown to effectively reduce nitrogen loads (Boyer et al. 2002, Osborne and Kovacic 1993, Pinay and Decamps 1988, Schoonover and Williard 2003) in the piedmont and coastal areas and are now considered an essential best management practice (BMP) for reducing the nitrogen load by 25 percent towards the restoration of the Chesapeake Bay (CBP 2019). As a result, Maryland developed a goal to plant about 40,000 ha of riparian forest buffers to achieve the Bay's Total Maximum Daily Loads (TMDLs) by 2025 (Maryland Department of Natural Resources 2019a). The estimate of 40,000 ha was calculated using statistical models that incorporate nutrient reduction loads using BMPs from the literature and current estimations of annual nutrient discharges (Verstraeten et

al. 2006, USDA and FSA 2011, Chesapeake Bay Commission 2016). These developed models have been shown to be reasonably reliable in some physiological provinces, such as the Coastal Plain and Piedmont, but become more inaccurate when applied to locations in the Appalachian Highlands physiographic provinces (Weller et al. 2011), including the Ridge and Valley (R&V) and the Appalachian Plateau. More accurate estimates of nutrient reduction in these areas are necessary, as the R&V and the Appalachian Plateau make up 60% of the Chesapeake Bay watershed (CBW) (Lowrance et al. 1997), extending across New York, Pennsylvania, Maryland, Virginia, and West Virginia. Verifying the factors that influence riparian forest function could reduce uncertainty when applying models to various regions and help water resource managers and organizations install BMPs in regions where efficiency is maximized.

Hydrological characteristics, including water table depth and subsurface flowpath, have been shown to strongly influence the function of riparian forests (Vidon and Hill 2004) and are unique to each physiographic province in the CBW (Lowrance et al. 1997). The water table's configuration is influenced by watershed position, local topography, and depth to an underlying aquitard (Vidon and Hill 2006, Mason et al. 2016). Nutrient reduction estimates are most reliable in the Inner Coastal Plain where the regional water table consistently occurs within the plant rooting zone of these low-lying flatlands (Lowrance et al. 1997, Messer et al. 2012), and in many instances, denitrification is the primary mechanism of nitrate removal within riparian buffer regions (Lowrance et al. 1997, Dhondt et al. 2003).

Nitrate-enriched groundwater interacts with denitrifying bacteria within a carbon-rich rhizosphere across broad landscapes, where some locations exhibit higher

denitrification activity than others (Böhlke and Denver 1995, Hill 1996, Lowrance et al. 1997, Gold et al. 1998). For instance, one study performed in the Nomini Creek watershed in the Coastal Plain found nitrate reduction ranges from 16 to 72%; higher nitrate reduction rates were observed in low topographic sites with shallow water table depths, with lower reduction rates reported for sites containing steeper slopes (Snyder et al. 1998). The authors hypothesized that sites with steep slopes have lower retention because of the rapid movement of groundwater, resulting in a short residence time that limits interactions between biologically active microbes and nutrients within the soil. P retention was more difficult to explain, however, since no correlations with slope or any of the other measured parameters (i.e., temperature, conductivity, and pH) were reported (Snyder et al. 1998). These results support the concept that regions such as the R&V, characterized by greater topographic relief, provide landscapes less conducive for nutrient mitigation through interception (Jacobs and Gilliam 1985, Pinay and Decamps 1988, Jordan et al. 1993, Lowrance et al. 1997, Schoonover and Williard 2003). Furthermore, Lowrance *et al.* (1997) hypothesized that soils in the R&V with high hydraulic conductivity, where groundwater seeps into deeper groundwater flowpaths, have the potential for nutrients to bypass the root system of a riparian forest before discharging into streams. Karst landscapes, found throughout the R&V, present a complex hydrological system comprised of sinking streams, springs, and fractured bedrock (Gburek and Folmar 1999a, White 2002, Pronk et al. 2009, Husic et al. 2019) that may affect riparian forest function and the potential for denitrification (Fig. 2.1).



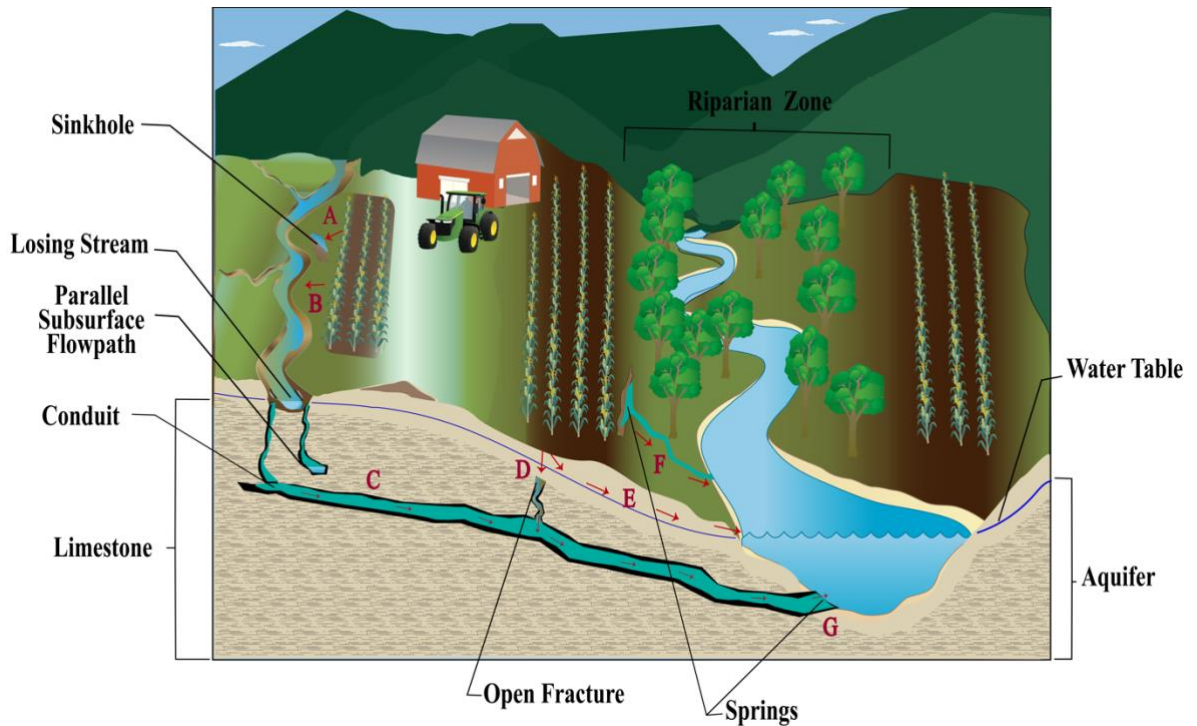


Figure 2.1 Conceptual Diagram of karst features and the different means nutrient rich waters from agricultural fields are transported from catchment to surface waters that can affect buffer function. Different transportation means include: (A) from agricultural field to a sinkhole that is connected to a cave or caverns; (B) direct discharge into streams where riparian vegetation is lacking; (C) subsurface conduit recharged by nutrient rich surface waters (e.g., via a losing stream); (D) water infiltrated into the soil and entering subsurface conduits via fractures in the bedrock; (E) water infiltrated into the soil and following a shallow subsurface flowpath through the rhizosphere; (F) groundwater discharging via soil macropores as a spring that generates surface flow as a small stream or rivulet into a larger stream; and (G) a spring discharging into a stream below the local water table. Scenario E provides the greatest potential for nutrients to be reduced by a riparian forest buffer.

Catchments with shallow subsurface flowpaths must also contain an available carbon source along with nitrate, favorable ranges of temperature, oxygen, and pH, and the presence of microorganisms in the soils to create an environment favorable for denitrification (Jacobs and Gilliam 1985, Pinay and Decamps 1988, Lowrance 1992, Jordan et al. 1993, Schoonover and Williard 2003). In regions where denitrification reduced nitrate, vegetation was the source of organic carbon, which emphasizes the importance of riparian buffers in reducing nutrients even without direct plant uptake (Lowrance 1992, Hefting and De Klein 1998, Martin et al. 1999b). However, another

study found nitrate to be higher in a catchment containing more organic matter, inferring that this led to a favorable environment conducive to net nitrate production from mineralization and nitrification. Nonetheless, this was also a consequence of specific soil moisture conditions (i.e., aerobic vs. anaerobic) and high levels of  $\text{NH}_4\text{-N}$  (Takatert et al. 1999).

Riparian zones have the greatest impact on the chemistry of ground and surface waters when stream-riparian zones, with sub-oxic conditions, develop microbially active areas and the residence time of the solutes is long enough for biological processes to take place (Gu et al. 2012). Biological nutrient removal processes that occur in the hyporheic zone — the region beneath and beside the stream bed — is a function of both hydrologic and soil characteristics, and the processes depend on soil water content, redox potential, and nutrient supply (Triska et al. 1993, Boyer et al. 1997, McClain et al. 2003, Vidon and Hill 2004, Gu et al. 2012). It has been verified with empirical data and models that high biogeochemical activity occurs in the near-stream riparian zone, depending on stream stage fluctuations (Gu et al. 2012, Gardner et al. 2016).

Nutrient mitigation and denitrification activity may also depend on underlying geology (Schnabel et al. 1997) and the watershed's hydrogeological setting. For example, one study compared grassed and forested buffer sites, along with the underlying geology (i.e., limestone or shale). The study found higher denitrification rates for grassed riparian buffer strips compared to forested. Results comparing the underlying geology only found significant differences amongst the limestone sites and no significant results between limestone and shale sites. None of the tested covariates (abundance of nitrate-N, organic carbon, or soil moisture) explained the significant differences between the limestone

sites, implying that geology impacts denitrification in some manner (Schnabel et al. 1997). Contrary to these results, another study within the Great Valley located in the R&V of the CBW demonstrated that chemical species and aqueous characteristics, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , pH, total alkalinity, and conductivity, are influenced by carbonate bedrock, but concentrations of N, dissolved organic P, dissolved organic matter, and  $\text{K}^+$  in streams were unaffected by the presence of carbonate rocks (Liu et al. 2000). Hydrologic flowpath has been hypothesized as the best predictor of nutrient mitigation from biological processes regardless of physiographic province (Schnabel et al. 1997, Schoonover and Williard 2003), although this hypothesis has not been widely tested.

Here we examined the mitigation of nutrient runoff across the R&V physiographic province by riparian forests through reach-based stream water quality surveys that considered the presence/absence of riparian forests, including both natural and planted forested buffers. The role of the local hydrogeological setting, especially the presence of mapped karst features, was hypothesized to influence the interactions between groundwater and surface water and thus the performance of riparian forests. Therefore, we considered groundwater discharge/recharge behavior at the scale of the individual stream reach. Interaction between groundwater and surface waters in stream reaches was hypothesized to influence stream water quality in response to land use/landcover (LULC). Finally, since all riparian forests are not equivalent in terms of geographic extent and canopy density, we also examined how these characteristics affected buffer performance across the region.

## ***2.3 Materials and methods***

### **2.3.1 Study region**

We evaluated riparian water quality functions across the Ridge and Valley (R&V) physiographic province of Western Maryland, specifically within several major tributary basins of the Potomac River. This physiographic province comprises 32% of the entire Chesapeake Bay watershed (area = 53,120 km<sup>2</sup>). Within the R&V, 60% of the province is presently forested, 26% is comprised of pasture and cropland, 11% is residential and roadways, and the remaining 3% is open water, barren land, and wetlands (USDA National Agricultural Statistics Service 2018). The Appalachian R&V geology largely consists of adamantine ridge capstones, including siliceous sandstone and conglomerates. The deeper bedrock and valley bottoms consist of limestone and shales that easily erode through chemical dissolution and fluvial processes (Fenneman 1938, Lowrance et al. 1997). In some regions, extensive erosion has led the formation of karst terrain, including a network of largely unmapped caverns and caves that enhances hydraulic conductivity and produces numerous springs and seeps throughout the project area (Grumet 2000). Caves are quite common in this part of western Maryland (Maryland Geological Survey 2015) with some located as close as 3.5 km to the study sites (Brezinski 2013).

### **2.3.2 Riparian/ Eco-hydrologically area (EHA)**

Defining optimal riparian buffer width for nutrient and sediment retention has become a popular research focus. Most studies have found the wider the buffer, the greater the nutrient and sediment retention (Mayer et al. 2007, Orzetti et al. 2010). However, little emphasis has been placed on whether the vegetation serving as a riparian buffer are within the riparian boundaries. Many of the nutrient and sediment retention

mechanisms of riparian buffers are dependent on the hydrogeomorphological characteristics specific to the riparian landscape ((Sidle and Onda 2004). When buffer width extends beyond the riparian region, it may have little effect on nutrient reduction, especially soluble forms in groundwater. Research on the hydrological network within the riparian area, which connects uplands to waterways, emphasizes the importance of the biological and chemical mechanisms and exchange of water and nutrients through bidirectional flows in this region (Triska et al. 1993, Merrill and Tonjes 2014). The biological and chemical mechanisms that retain nutrients depend on a shallow subsurface flowpath where the large amount of variation in forest nutrient retention often observed is assumed to be related to the lack of surface- and groundwater interactions. For instance, wide buffers are recommended in regions with steeper slopes, but this has only shown significant reductions in sediment and phosphorus (Schmitt et al. 1999, Abu-Zreig et al. 2003, Lee et al. 2000) with no significant reductions of N (Mayer et al. 2005, Zhang et al. 2010, Valkama et al. 2019). While numerous studies have highlighted that complex subsurface stratigraphy makes it difficult to predict riparian function (Schiff et al. 2002, Böhlke et al. 2007, Ator et al. 2015), we explored a novel approach of estimating the area of each riparian zone that supports shallow groundwater using remote sensing.

Subtle topographic gradients discernible from high resolution elevation data can provide an adequate first-order indication of the dominant hydro-geomorphic controls on biogeochemical processes across a landscape (Richardson et al. 2010) and throughout entire catchments (Murphy et al. 2008, 2009). We defined the riparian area as an active ecohydrological area (EHA) using high-resolution topography data to map wetland, stream, and river morphologies shaped by near-surface ground- and surface-water

interactions and subsequently identified where denitrification, sedimentation, or stream bank erosion likely influence water quality. This was performed by first developing a high-resolution stream map using Light Detection and Ranging (LiDAR) derived digital elevation models (DEMs) with 1 to 2 m pixel resolution and assuming (1) perennial surface water features represent an outcrop of the water table (Winter et al. 1998); and (2) adjacent areas within 1.5 m elevation (i.e., the plant rooting zone) have a greater probability of shallow water table conditions that can sustain biogeochemical and biophysical processes (Fig. 2.2). LiDAR is a powerful tool for mapping topography and identifying landforms that might be expected to serve particular ecosystem functions. The slope across the width of the EHA area was used to evaluate the relative importance of ground- versus surface-water in controlling hydrochemical reactions across a site. For instance, shallow-sloping topographic gradients (3 to 15 percent) indicate that sustained advective groundwater flow likely provides a delivery mechanism for shallow, contaminated waters and thus where there exists greater potential for N removal via denitrification (Vidon and Hill 2004). Flatter areas adjacent to surface water features indicate where overbank flooding likely sustains wetland conditions, including enhanced sedimentation, but also where the lack of advective groundwater flow (i.e., flat hydrologic gradient) likely limits denitrification rates, even if ideal conditions occur (i.e., organic-rich, reduced soils). Steeper sloping, often more narrow EHA areas, likely indicate stream incision and where groundwater has a greater likelihood of by-passing biologically active, organic-rich root zones, thus limiting nutrient loss by denitrification and/or exacerbating streambank erosion and entrenchment rather than floodplain sediment deposition (Seitzinger et al. 2006, Böhlke et al. 2007, Hupp et al. 2009).

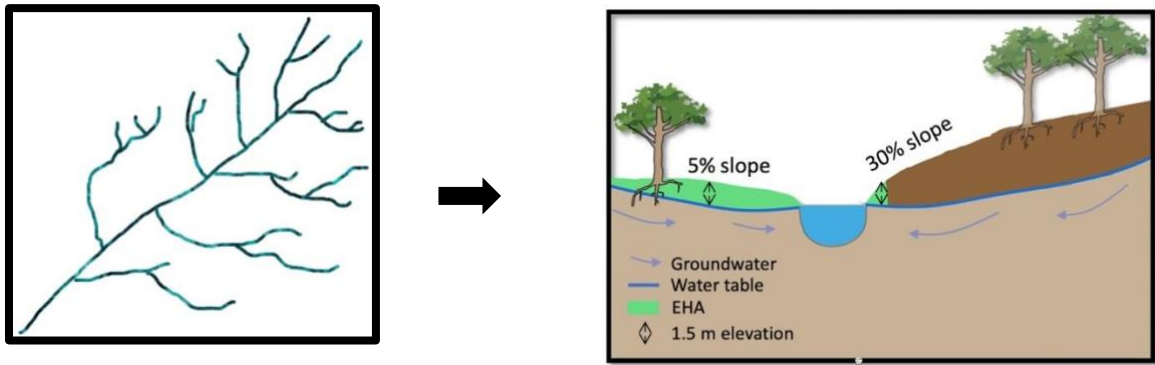


Figure 2.2 Conceptual diagram showing the sequence of how ecohydrological areas (EHAs) were identified and what landscape characteristics were considered when hypothesizing which regions of watersheds are conducive to biological processes.

### 2.3.3 Reach survey design

The target population of low-order stream reaches (“segments”) were located in the R&V province of western Maryland in Allegany County (ALCO) and Washington County (WACO) (Fig. 2.3). Sites were selected from the counties separately because the Conservation Reserve Enhancement Program (CREP), a program that pays landowners to install best management practices (BMP), is implemented on a county level and landowners receive different incentives based on county soil rental rates (Maryland Department of Natural Resources 2019a). For all surveys, we focused exclusively on 3<sup>rd</sup> and 4<sup>th</sup> (Strahler) order segments shown on a stream network map developed by Elmore et al. (2013) after a pilot survey conducted on one ALCO subwatershed in 2013 found that all 1<sup>st</sup> and 2<sup>nd</sup> order segments were dry under spring baseflow conditions. Segments that had local contributing areas (LCA) smaller than 5% of the total contributing area (TCA) or that had >4% impervious surface area, based on the National Land Cover Database (NLCD), were eliminated, resulting in a final target population comprised of

396 segments in ALCO and 287 segments in WACO. TCA is the total drainage basin to the downstream outlet and LCA is the difference between the two drainage basins of the upstream and downstream outlet. TCA was calculated for each downstream station using TauDEM software package and 10 m DEMs base data from U.S. Geological Survey, 2017 (1/3<sup>rd</sup> arc-second DEMs from USGS National Map 3DEP Downloadable Data Collection: U.S. Geological Survey). The National Hydrography Dataset (NHD) was used to “burn” the flow paths into the DEM — a process in which the NHD flow path is enforced by artificially lowering the elevation under the vector stream file. The contributing area upstream of each reach (determined using the same method) was subtracted from the contributing downstream area (i.e., TCA) to calculate LCA.

Finally, by overlaying an EHA layer onto a map of forest and non-forest, again based on the NLCD, we computed differences in the areas of non-forested and forested EHA in the LCA of each segment (overall range -99% to 68%) that were then “binned” into one of 16 bins (strata) that spanned the range. This was done for each county to obtain a proportional number of sites from each bin. Four segments from each bin were randomly selected, with one site purposefully identified for field sampling based on ease of access; the other three sites were used as backups if field sampling was not possible (i.e., reach was dry, access permission for sampling wasn’t granted, etc.). To account for the stratified random design, we computed weighted averages for some variables as follows:

$$\chi_{average} = \frac{[\sum(x*n_i)]}{\sum n} , \quad (1)$$



where  $x$  is the variable of interest measured in each reach,  $n_i$  is the number of segments found in the watersheds within each bin, and  $n$  is the total number of sites in all 16 bins. Of the 32 segments (i.e., “sites”) we identified for field sampling, we were only able to successfully sample 25 (14 sites in ALCO, 11 sites in WACO); we were unable to find suitable sites in several bins that comprised the tails of the EHA distribution. Hereafter we refer to the two stratified random surveys by the acronyms “ALCO” and “WACO” for the counties in which the surveys were conducted.

Due to the sparseness of riparian forests planted through CREP in western Maryland (i.e., none of the randomly selected sites included one of these buffers), we designed two complementary ‘special interest’ surveys focused on planted riparian forested reaches in each of the two counties under CREP. First, CREP buffers were digitized in ArcGIS by referencing CREP records obtained from Maryland DNR of hard copy maps. In Allegany County, riparian forests occupied 235 hectares of land (87 separate plantings) and in Washington County, riparian forests covered 298 hectares (77 separate plantings). Fourteen ALCO sites and 17 WACO sites that included planted riparian forests were selected from the original target population primarily based on accessibility. We subsequently refer to these surveys by the acronyms “ALSI” (Allegany County Special Interest) and WASI (Washington County Special Interest). Most of the riparian forests within the selected ALSI and WASI segments were planted in 2003 (range between 2000 and 2013) and 2002 (range between 1997 and 2013), respectively. We also observed nearly perfect, albeit anecdotal, agreement between the mapped areas of planted buffers and the actual areas on the ground (Fig. 2.3).

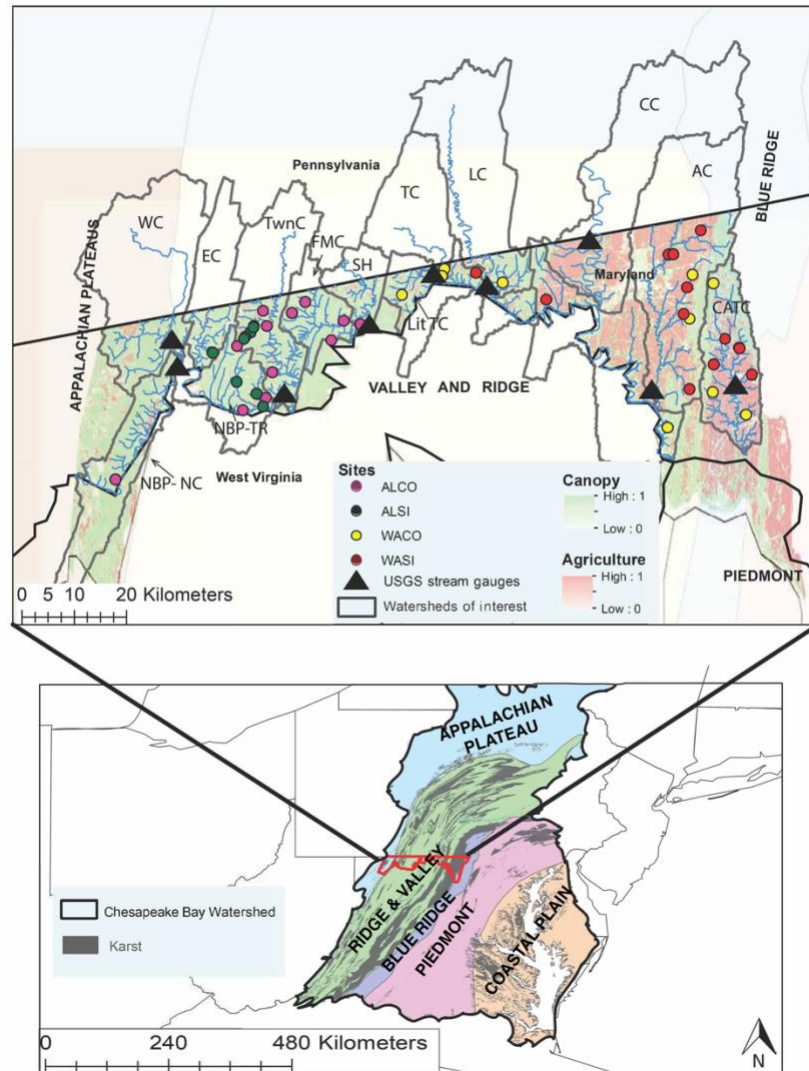


Figure 2.3 Map of study sites in western Maryland in reference to entire Chesapeake Bay watershed (CBW) shown in the bottom map with physiographic geological provinces. Washington and Allegany Counties are highlighted in red, which is the location of our study sites. Map indicates location of the Ridge and Valley (R&V) throughout the entire CBW (green). Karst is also indicated in gray to demonstrate how prominent this landscape is in the R&V. Specific watersheds, study sites, and location of USGS gauges are shown in the zoomed-in, upper map. ALCO and WACO refer to study sites selected randomly in Allegany and Washington Counties respectively. ALSI and WASI refer to study sites specifically selected for their planted riparian forest buffers through the Conservation Reserve Enhancement Program in Allegany and Washington Counties respectively. Canopy and agriculture are shown on the map in the green and red coloration respectively. Watersheds are Wills Creek (WC); Evitts Creek (EC); North Branch Potomac- New Creek (NBP-NC); North Branch Potomac- Trading Run (NBP-TR); Town Creek (TwnC); Fifteenmile Creek (FMC); Sideling Hill Creek (SH); Tonoloway Creek (TC); Little Tonoloway Creek (Lit TC); Licking Creek (LC); Conococheague Creek (CC); Antietam Creek (AC); and Catoctin Creek (CATC). Landuse layer shows Washington County has more agriculture (eastern county) than Allegany County (western county).

### 2.3.4 Field and laboratory methods

We assessed riparian forest function in reducing nutrient pollution through field measurements made at the upstream and downstream ends of the selected reaches under baseflow conditions during the spring (May through June) of 2014. Stormflow conditions were avoided by referencing hydrographs on the United States Geological Survey (USGS) website of gauged basins within the survey area (i.e., Town Creek, Sideling Hill Creek, and Antietam Creek). Each segment was sampled once (both upstream and downstream ends on the same day and sequentially to reduce variability in hydrologic conditions during the sampling period). Surveys included the collection of streamwater “grab” samples in 1-L polyethylene cubitainers<sup>®</sup> and instantaneous streamflow measurements using a Marsh-McBirney Flo-Mate<sup>™</sup> electromagnetic current meter and a wading rod (mid-section current meter method of USGS, 2015). Samples were immediately placed on ice and returned to the lab for processing.

Filtering occurred within 24 hours of collection using the vacuum filtration (<10 psi vacuum) method using 0.45 µm membrane filters. Aliquots of filtered water were placed into 125 ml plastic sample bottles and stored at 4°C until analysis within pre-established holding times. Holding times followed standard EPA (1999) and APHA (1998) methods (Chanlett 1947, O’Dell 1996, Kline 2013). Samples were analyzed for nitrate-N (NO<sub>3</sub>-N), ammonium-N (NH<sub>4</sub>-N), orthophosphate-P (PO<sub>4</sub>-P), total dissolved nitrogen (TDN), total dissolved phosphorus (TDP), dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) in mg/L by colorimetry using a Lachat QuikChem 8000 flow injection analyzer. Dissolved organic nitrogen (DON) and phosphorus (DOP) were calculated as the difference between TDN and NO<sub>3</sub>-N and NH<sub>4</sub>-

N, and TDP and PO<sub>4</sub>-P, respectively. Laboratory duplicates, blanks, calibration checks, and control samples were used to ensure the quality of the analytical results.

### **2.3.5 Defining catchment area, land use, & geological features**

Study sites (segment “ends”) were marked in the field using a Garmin eTrex 20 Global Positioning System (GPS) and uploaded into ArcGIS as waypoints. Field points from the GPS were “snapped” to match the stream segments. TCA and LCA were again recalculated for these specific sites using the previously described methods under section *Reach Survey Design*. LCA land use properties (e.g., canopy cover, agriculture, biomass) were determined using 10 m resolution maps obtained from the Department of Geological Sciences at UMD. Land use was calculated in TauDEM using the FAC tool with each of the LULC rasters used as the optional weight (Tarboton et al. 2009). Cropscape Data Layer from 2014 (USDA National Agricultural Statistics Service 2018) was used to define specific agricultural land uses that were needed to model nutrient concentrations in the LCAs. Shapefiles of subwatersheds used with a 30 m Cropscape Data Layer were delineated using Archydro tools and a flow accumulation raster where preprocessing was performed with the TauDEM software package (Tarboton et al. 2009). Location of karst was determined using US Karst Map that was downloaded from USGS website (Weary and Doctor 2014) and uploaded onto ArcGIS map that contained study site locations. Any site with part of the LCA containing karst was categorized as ‘karst present’. The US Karst map was created by compiling multiple sources from different spatial scales and based on karst potential – bedrock geology, tectonics, climate, sedimentary cover, vegetation, local hydrologic conditions, and time, as well as areas containing soluble bedrock lithologies that have the potential to host karst features

(Weary and Doctor 2014). Although the karst map may lack accuracy, it is the best available data that we could acquire for this study.

### 2.3.6 Hydrologic analysis

#### *Hydrological characterization*

Lateral groundwater discharge from the LCA ( $Q_{lat}$ ) was calculated as

$$Q_{lat} = Q_{meas,D} - Q_{meas,U} \quad (2)$$

where  $Q$  is volumetric flow rate ( $m^3/s$ ), and subscripts  $D$  and  $U$  connote downstream and upstream, respectively. Computed values were used to categorize reaches as net losing ( $Q_{lat} < 0$ ) or gaining ( $Q_{lat} > 0$ ) under baseflow conditions. Volumetric flow rates were measured once due to time and accessibility; therefore, to address the uncertainty of our measurements, we incorporated a  $\pm 5$  and 10% error (i.e., multiplied factors 1.05 and 1.1 to  $Q_{meas,D}$ , respectively and 0.95 and 0.9 to  $Q_{meas,U}$ , respectively) to the flow balance equation (eq. 2) to confidently determine which reaches were losing and estimate how much a 5 and 10% error would influence our results. Five and 10% were used because most discharge measurements have indicated a 3 to 6% standard error under conditions similar to our study (no shortcuts taken, use of calibrated equipment, measurements taken in a stable streambed, etc.) and we used the mid-section method where computational errors are usually small (Sauer and Meyer 1992). Although none of the 56 reaches were gauged, at least one stream located within the nine subwatersheds was gauged by USGS (Fig. 2.3). Data from the closest gauging station to each reach was used to estimate the baseflow discharge ( $\hat{Q}$ ) at the reaches upstream and downstream ends, assuming that mean daily discharge in these systems scales proportionally to TCA. Lateral groundwater discharge ( $\hat{Q}$ ) from each reach was then calculated:

$$\hat{Q}_{lat} = \hat{Q}_D - \hat{Q}_U \quad (3)$$

where, again, subscripts *D* and *U* connote downstream and upstream, respectively.

Linear regression was used to determine how well the predicted baseflow discharge matched the corresponding observed discharge. Linear Regression model assumptions (i.e., global stat, skewness, kurtosis, link function, and heteroscedasticity) were validated using the *gvlma* package in R (Peña and Slate 2006). The Kruskal-Wallis Test was used to assess the significance between the residuals of observed and predicted discharge rates of the study sites with and without karst presence.

#### *Nutrients and land use*

Differences in raw nutrient concentrations (i.e.,  $\Delta C = C_D - C_U$ ) and estimates of the nutrient concentrations in the lateral groundwater inflow ( $C_{lat}$ ) were analyzed to test if stream water quality is (1) impacted by variation in ground- and surface-water exchange, (2) a function of LULC, and (3) dependent on whether streams are dominated by groundwater, as opposed to springs, for the riparian forests to function optimally.

Nutrient concentrations of net groundwater lateral inflow ( $C_{lat}$ ) could not be calculated for reaches with negative  $Q_{lat}$ ; therefore, losing reaches were omitted (25 sites total: 10 from Allegany Co. and 15 from Washington Co).  $C_{lat}$  for gaining reaches was quantified using a steady-state reach mass balance model that neglects in-stream processing:

$$C_{lat} = \frac{(Q_D * C_D) - (Q_U * C_U)}{(Q_D - Q_U)} \quad (4)$$

In some instances,  $C_{lat}$  values were negative when upstream and downstream flow rates were within close range and the nutrient concentrations downstream were lower, possibly from in-stream processing and/or measurement error. Since one grab sample was

collected from each end of the reach (i.e., upstream and downstream), the uncertainty was calculated again using the  $\pm 5$  and 10% error criteria. The probable error range for dissolved nutrients ranges from  $\pm 0\%$  to 2% when samples are stored in ice 6 hours prior to analysis and  $\pm 2\%$  to 16% when samples are refrigerated for 54 hours prior to analysis (Harmel et al. 2006). Because stringent analytical procedures were followed after samples were collected, where the full description can be found under *Field and Laboratory Methods*, we confidently assumed that the error range did not exceed 10%.

Riparian forest function was assessed by (1) a combined analysis of ‘special interest’ and ‘random’ sites and (2) analysis of the ‘special interest’ sites separately. A combination of tests was used to explore significant relationships between LULC (% canopy within the LCA, % forested EHA, and % planted buffer in LCA) and nutrient concentrations (i.e.,  $C_{lat}$  and  $\Delta C$ ) using Spearman’s Rank Correlation (SRC) Test because of the non-normal distribution of the data and small sample size. Rather than looking only at LULC conditions within a static buffer width, the EHA analysis allowed us to estimate riparian width based on predicted depth to water table and where the water table depth from the surface likely occurs within the rhizosphere. We investigated a possible threshold of percentage forested EHA needed for nutrient reduction by dividing sites into bins with assigned ranges of percent forested area within their EHA (i.e., 1-25%; >25-50%; >50-75%; and >75-100%) and tested against  $\Delta C$ , including all sites (gaining and losing reaches) and  $C_{lat}$  (gaining reaches only), using the Kruskal-Wallis test. Nutrient declines in ‘special interest’ sites (gaining reaches only) were assessed by examining significance between paired upstream and downstream nutrient concentrations using a Welch Two Sample T-test. We tested the effect of losing reaches on  $\Delta C$  using a one-

sample  $t$ -test. We hypothesized that concentrations remain consistent from upstream to downstream ( $\Delta C=0$ ) since, presumably, losing reaches receive little groundwater inputs, and the stream is recharging groundwater.

A survey-weighted SRC Test within the “wCorr” R-package (version 1.9.1) (Emad and Bailey 2017) was used to analyze the change in response of nutrients to percent canopy in LCA and percent forested EHA using a better representation of reach populations based on the weights described in the *Reach Survey Design* section. By repeating our analyses in this manner, we assumed that giving more “weight” to catchments that are more commonly found throughout Allegany and Washington Counties (based on the forested EHA) would provide a better indication of how the counties, overall, are more likely to be influenced by land cover. Stronger relationships between nutrient concentrations and percent canopy or forested EHA would then indicate that riparian areas with similar LULCs respond analogously, implying that forest management can be implemented on a catchment scale rather than a reach scale (Kuglerová et al. 2014).

Because it is unclear if mature or young forest are more efficient at reducing nutrients (Broadmeadow and Nisbet 2004, Parkyn 2004, Mayer et al. 2007, Orzetti et al. 2010), ANCOVA was used to determine if the response of nutrients ( $C_{lat}$ ) to percent forested EHA was affected by the two site categories (i.e., special interest and random).

#### *Modeling nutrient concentrations*

To assess how well LULC explains stream nutrient concentrations and to determine if nutrient levels can be predicted within our research sites, we tested two empirical models: (1) The Nature Conservancy (TNC) model and (2) a model developed



by Gburek and Folmar (1999). The TNC model is used to identify optimal locations for buffer restoration based on the Chesapeake Bay Program (CBP) predicted loading rates for specific LULCs, a DEM-based surface flowpath analysis, and EHA mapping (Boomer, unpublished). The model uses edge-of-stream loading rates that were specifically calculated for the LULCs in each of the counties in Maryland. Loading rates were then multiplied by the appropriate LULC in the subcatchments to estimate annual loads. The second model, developed by Gburek and Folmar (1999), predicts NO<sub>3</sub>-N (mg/L) in small watersheds in the R&V province, using the following equation:

$$\text{NO}_3\text{-N (mg/L)} = [(1.0) (\% \text{forest}) + (8.0) (\% \text{crop rotation}) + (20.0) (\% \text{corn}) + (10.0) (\% \text{pasture}) + (30.0) (\% \text{animals})] / 100, \quad (5)$$

where specific coefficients are multiplied by a set of land use variables included in the Cropscape data layers. Coefficients for other crop types in our watersheds were chosen based on common farming practices for each crop relative to the growing techniques used for corn and its assigned coefficient given in this model (Gburek and Folmar 1999b).

## **2.4 Results**

Across all sites, the fraction of forested EHA and canopy in the LCA exhibited a negative effect on measured stream nutrient concentrations, but this effect was not observed at ‘special interest’ sites (Table 2.1A/B). Both  $\Delta\text{PO}_4\text{-P}$  and  $\Delta\text{TDP}$  declined with increasing percent canopy and forested EHA at ALCO sites (p-value < 0.05, Table 2.1A/B); however,  $\Delta\text{TDP}$  increased with increasing percent forested EHA at WASI sites ( $\rho=0.52$ , p-value < 0.05, Table 2.1B). No relationships were found at the ALSI sites or WACO sites in the  $\Delta C$  analysis. This statistical analysis had limited utility because it incorporated both losing and gaining reaches. The medians of  $\Delta C$  of losing reaches were

not significantly different from zero, except for NO<sub>3</sub>-N and TDN for all sites and TDN for ALSI sites only (p-value < 0.05). The 95% confidence intervals hypothesized medians less than zero, indicating a loss of nutrients.

Analyzing gaining reaches only, LULC exhibited effects on  $C_{lat}$  values. This result was strongest at ALCO sites, demonstrating that in Allegany County an increase in percent canopy and an increase in forested EHA was associated with lower  $C_{lat}$  values as we expected (Table 2.1A/B). WACO sites also exhibited reduced nutrient levels (PO<sub>4</sub>-P and TDP) at sites with higher canopy cover, showing the largest effect compared to the other sites ( $\rho = -0.89$  and  $-0.94$ , respectively, Table 2.1A). No relationships were found at the ‘special interest’ sites when analyzing them separately for either county. While these statistical models demonstrate multiple negative relationships between percent canopy/forested EHA and nutrient concentrations when incorporating all sites together, we consider these relationships weak ( $\rho$  ranged from  $-0.36$  to  $-0.52$ , Table 2.1A/B). We further recognize that the responses may not simply be a consequence from the presence of a buffered riparian area but from an increase in upland forests that release less nutrients compared to agricultural fields — a result shown in some of the single survey (i.e., ALCO) analyses as well.

Performing analyses using the two categories (i.e., ‘randomly selected’ and ‘special interest’ sites) confirmed that nutrient concentration responses to LULC were greater for the ‘randomly selected’ sites compared to the ‘special interest’ sites. Nevertheless, the results described thus far were unweighted and may misrepresent nutrient removal efficiency of riparian buffers in the R&V. Using the R package ‘wCorr’, the correlation coefficient ( $\rho$ ) of SRC was calculated again using the weights described in

the methods section, that was based on the amount of forested and non-forested EHA in the LCA of each segment (Emad and Bailey 2017). We assume that the response of nutrient removal from the selected reaches of each bin, which are based on the percentage of forest within their adjacent EHA, accurately represents how the other reaches in that bin would respond. Relationships between  $C_{lat}$  of TDN/TDP and percent canopy and forested EHA are described by scatterplots (Fig. 2.4). Compared to the unweighted model, the weighted analysis produced a higher  $\rho$  using SRC tests, indicating a stronger relationship between LULC and nutrient concentrations (i.e., TDN<sub>clat</sub> vs. % canopy:  $\rho_{unweighted} = -0.70$ ;  $\rho_{weighted} = -0.81$ ; TDN<sub>clat</sub> vs. % forested EHA:  $\rho_{unweighted} = -0.32$ ;  $\rho_{weighted} = -0.37$ ; TDP<sub>clat</sub> vs. % canopy:  $\rho_{unweighted} = -0.78$ ;  $\rho_{weighted} = -0.89$ ; TDP<sub>clat</sub> vs. % forested EHA:  $\rho_{unweighted} = -0.61$ ;  $\rho_{weighted} = -0.66$  shown in Fig. 2.4). These results imply that reaches more commonly found throughout the watershed have a greater response to landuse and forested riparian areas than those less typical. However, because of the heterogeneity across the landscape, we are skeptical that one reach per bin accurately exemplifies all the other reaches.

Table 2.1 Spearman’s Rank Correlation (SRC) results showing relationships between  $\Delta C$  (raw nutrients) and  $C_{lat}$  (nutrients in lateral groundwater) (dependent variables) versus % canopy (A) and % forested EHA (B) (independent variables) across four subwatersheds. Analyses were performed by combining all subwatersheds together (‘All Sites’) and individually (‘ALCO’, ‘ALSI’, ‘WACO’, and ‘WASI’). ‘ALCO’ and ‘ALSI’ are sites located in Allegany County that were randomly and specifically selected respectively. ALSI sites were specifically selected because they contained planted riparian forest buffers through the Conservation Reserve Enhancement Program. ‘WACO’ and ‘WASI’ were selected using the same criteria as ‘ALCO’ and ‘ALSI’, respectively, but were located in Washington County. SRC results of  $\Delta C$  (upper rows) incorporated all reaches (losing & gaining) and  $C_{lat}$  (lower rows) incorporated gaining reaches only. Statistically significant values (p-value < 0.05) are indicated in bold, blue font and “n” refers to the number of sites in each category.

		All Sites		ALCO		ALSI		WACO		WASI	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b><math>\Delta</math>, gaining/losing reaches</b>	NO <sub>3</sub> -N	0.23	-0.16	0.10	-0.46	0.67	-0.13	0.67	0.15	0.33	-0.25
	NH <sub>4</sub> -N	0.49	-0.09	0.20	-0.37	0.86	-0.05	0.55	0.20	0.46	0.19
	TDN	0.22	-0.17	0.19	-0.38	0.80	0.08	1.00	0.00	0.63	-0.13
	DON	0.91	-0.02	0.82	-0.07	0.18	0.38	0.36	-0.31	0.11	0.40
	PO <sub>4</sub> -P	0.69	-0.05	<b>3.5E<sup>-02</sup></b>	<b>-0.56</b>	0.68	-0.12	1.00	0.00	0.76	0.08
	TDP	0.50	-0.09	<b>9.3E<sup>-03</sup></b>	<b>-0.67</b>	0.48	0.21	0.92	-0.04	0.46	0.19
	DOP	0.81	0.03	0.43	-0.23	0.64	0.14	0.99	-0.01	0.16	0.36
			<i>n</i> = 56		<i>n</i> =14		<i>n</i> =14		<i>n</i> =11		<i>n</i> =17
<b><math>C_{lat}</math>, gaining reaches only</b>	NO <sub>3</sub> -N	<b>2.0E<sup>-02</sup></b>	<b>-0.42</b>	<b>2.1E<sup>-02</sup></b>	<b>-0.73</b>	0.13	0.60	0.56	-0.31	0.78	0.14
	NH <sub>4</sub> -N	0.79	-0.05	0.66	-0.16	0.93	0.05	0.66	-0.26	0.24	0.54
	TDN	<b>5.2E<sup>-03</sup></b>	<b>-0.49</b>	<b>2.8E<sup>-02</sup></b>	<b>-0.71</b>	0.30	0.43	0.10	-0.77	0.78	0.14
	DON	0.35	-0.17	0.73	-0.13	0.88	0.07	0.36	-0.49	0.30	0.46
	PO <sub>4</sub> -P	<b>2.7E<sup>-03</sup></b>	<b>-0.52</b>	0.07	-0.60	0.15	-0.57	<b>3.3E<sup>-02</sup></b>	<b>-0.89</b>	0.78	0.14
	TDP	<b>8.5E<sup>-03</sup></b>	<b>-0.46</b>	<b>2.8E<sup>-02</sup></b>	<b>-0.69</b>	0.39	0.36	<b>1.7E<sup>-02</sup></b>	<b>-0.94</b>	0.71	0.18
	DOP	0.15	-0.27	0.56	-0.21	0.22	0.50	0.24	-0.60	0.71	0.18
			<i>n</i> = 31		<i>n</i> =10		<i>n</i> =8		<i>n</i> =6		<i>n</i> =7

B)

		All Sites		ALCO		ALSI		WACO		WASI	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b><math>\Delta</math>, gaining/losing reaches</b>	<b>NO<sub>3</sub>-N</b>	0.15	-0.19	0.28	-0.31	0.10	-0.46	0.99	-0.01	0.82	-0.06
	<b>NH<sub>4</sub>-N</b>	0.85	-0.03	0.12	-0.43	0.63	0.14	0.30	0.34	0.95	-0.02
	<b>TDN</b>	0.22	-0.17	0.50	-0.20	0.33	-0.28	0.50	0.23	0.67	-0.11
	<b>DON</b>	0.85	-0.03	0.93	0.02	0.80	0.08	0.86	0.06	0.57	0.15
	<b>PO<sub>4</sub>-P</b>	0.34	-0.13	<b>2.6E-02</b>	<b>-0.59</b>	0.87	-0.05	0.19	-0.42	0.31	0.26
	<b>TDP</b>	0.38	-0.12	<b>2.6E-02</b>	<b>-0.59</b>	0.82	0.07	0.48	-0.24	<b>3.1E-02</b>	<b>0.52</b>
	<b>DOP</b>	0.83	-0.03	0.25	-0.33	0.83	0.06	0.33	0.33	0.08	0.44
		n = 56		n=14		n=14		n=11		n=17	
<b>Clat, gaining reaches only</b>	<b>NO<sub>3</sub>-N</b>	<b>4.7E-02</b>	<b>-0.36</b>	0.14	-0.50	0.39	0.36	0.71	0.20	0.20	-0.57
	<b>NH<sub>4</sub>-N</b>	0.93	0.02	0.27	-0.39	0.98	-0.02	0.92	0.09	0.44	0.36
	<b>TDN</b>	<b>2.9E-02</b>	<b>-0.39</b>	0.17	-0.47	0.66	0.19	1.00	-0.03	0.20	-0.57
	<b>DON</b>	0.31	-0.19	0.74	-0.12	0.20	-0.52	1.00	0.03	0.71	0.18
	<b>PO<sub>4</sub>-P</b>	<b>4.3E-02</b>	<b>-0.37</b>	<b>3.9E-02</b>	<b>-0.66</b>	0.39	-0.36	0.14	-0.71	0.50	-0.32
	<b>TDP</b>	0.10	-0.30	<b>3.2E-02</b>	<b>-0.68</b>	0.67	0.19	0.10	-0.77	0.84	0.11
	<b>DOP</b>	0.35	-0.33	0.35	-0.33	0.75	0.14	0.24	-0.60	0.84	0.11
		n = 31		n=10		n=8		n=6		n=7	

Note: Dependent variables were expressed in mg/l during analysis.

The relationship between percent forested EHA and  $C_{lat}$  of TDN/TDP was weaker compared to the relationship with percent canopy. Scatterplots demonstrated an increase in nutrient concentrations along the mainstem and/or high amounts in tributaries and karst springs despite having high percentages of forested EHA. Further investigation discovered that these sites typically had low percent canopy in the local catchment. For instance, one outlier site containing 70% forested EHA (which is high) had a high  $C_{lat}$  of TDP, but low  $C_{lat}$  of TDN. We inferred that this was a likely consequence of 53% of the LCA being pasture. Therefore, despite some reaches having a high percentage of forested EHA, water quality may depend more on the upland land use.

Contrarily, when analyzing ALSI and WASI ('special interest' sites) results together, no relationships were found between % forested EHA (i.e., planted buffers) and stream nutrients, nor with % canopy cover and stream nutrients, except a positive relationship between  $\Delta$ TDP and % forested EHA amongst WASI sites. Several outliers from both surveys showed high nutrient concentrations, despite having a higher percent canopy and detection of forested FEHA. The results of the ANCOVA found no significant differences between the two site categories, except for  $C_{lat}$  of DON versus % canopy cover (p-value < 0.05). However, the residuals were not normally distributed, and one major outlier was detected. Once the outlier was removed, results were no longer significant. To investigate other factors and variables that may be influencing the function of riparian forests, we examined whether thresholds were present in the effect of forested EHA on stream nutrients ( $\Delta$ C and  $C_{lat}$ ). However, we found no significant change when dividing percent forested EHA into bins (1-25%; >25-50%; >50-75%; >75-100%). Age of the riparian forests was another variable that was tested, but no statistical

significance was found. We surmise that the quality of the stream is not an exclusive product of current landcover, but also subjected to a legacy effect from previous land use dependent upon the groundwater flowpath and residence time.

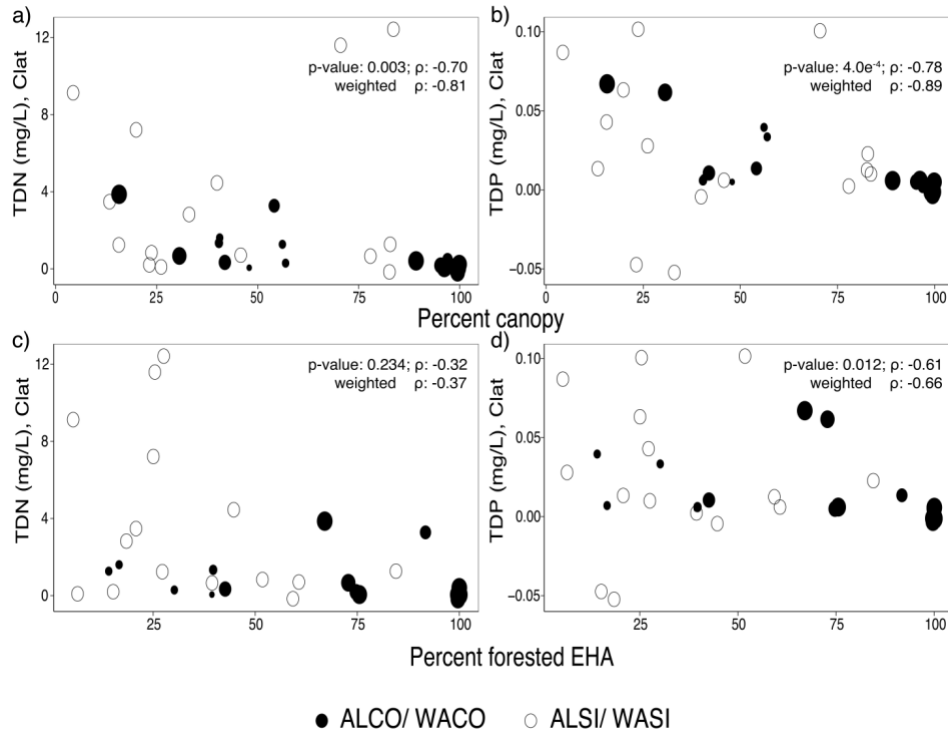


Figure 2.4 Flow weighted lateral groundwater concentrations of TDN and TDP (mg/L) (includes gaining reaches only) as a function of percent canopy in local contributing watersheds (a/b) and percent forested eco-hydrological area (EHA)/ riparian area (c/d). ‘Random sites’ (i.e., ALCO and WACO) and ‘special interest’ sites (i.e., ALSI and WASI) are represented by the solid and open circles, respectively. ‘Random sites’ are weighted based on the number of stream segments found in each watershed based on the forested EHA within the total contributing area. Larger symbols connote sites that are more heavily weighted/ more commonly found across each county. The probability (p-value) and correlation coefficient ( $\rho$ ) (unweighted and weighted) were found using Spearman’s Rank Correlation Test.

A hydrological investigation based on a comparison of measured and modeled (Eq. 3) stream discharges indicated that observed discharge was much better predicted for the Washington County reaches (i.e., WACO:  $R^2= 0.87$ , slope= 0.91; WASI:  $R^2= 0.93$ , slope= 1.0) than for the Allegany County sites (i.e., ALCO:  $R^2=0.22$ , slope=0.34; ALSI:  $R^2=0.30$ , slope= 0.61). Based on these results the complexity of the hydrological

pathways throughout the R&V was hypothesized to affect riparian forest function and stream water quality. Sites demonstrating the most ‘normal’ hydrological characteristics, based on the agreement between observed and predicted discharge rates, were expected to exhibit relationships between LULC and nutrient concentrations. However, Washington County had more losing reaches than Allegany County (Table 2.2), which is not considered a ‘normal’ characteristic and karst presence was not found to be a significant predictor for losing reaches — determined using residuals between observed and predicted discharge (Kruskal-Wallis Test p-value = 0.15). The prevalence of losing reaches may have attributed to the lack of significant relationships found between LULC and nutrients.

When plotting observed and predicted discharge, on a log-scale, for the two survey categories separately, ‘special interest’ sites produced better results than the ‘random sites’ (i.e., resulted in a higher  $R^2$  (0.67), met all linear regression assumptions, and produced a slope close to 1 (1.08) (Fig. 2.5A/B)). ‘Random sites’ contained a greater number of smaller streams with low discharge rates where the model performs more poorly. Streams with higher discharge rates may be easier to predict than smaller reaches; therefore, we tested this theory by redoing the analysis using ‘random sites’ with discharge rates greater than 3.22E-03 cms (the lowest discharge rate within the ‘special interest’ sites). This reduced the number of sites from 48 to 19, but it improved the model by finding a significant relationship (p-value<0.01) that met all linear regression assumptions with a high  $R^2$  (0.8) and slope close to 1 (1.09). Losing streams had the highest discharge rates in both survey categories where karst was present for only a few of these reaches. Using the Kruskal-Wallis test, the differences in residuals of observed



and predicted discharge rates between the two groups (i.e., karst and non-karst) were significant ( $p$ -value = 0.01) for the ‘randomly selected’ sites only. However, using boxplot as a visual tool showed ‘karst present’ sites were closer to 0 than those where karst was absent (i.e., mean difference between log observed and predicted discharge rates was -0.6 with karst and -1.8 without karst). Sites labeled as ‘karst absent’ showed more variability and outliers between the observed and predicted discharge (Appendix A). The ‘special interest’ sites had many more reaches within karst, but the log residuals between sites were not significant ( $p$ -value > 0.05). However, karst-present sites showed more variability than those without karst (i.e., mean log residuals were -0.8 and -0.4, respectively). Although it is difficult to isolate the effect of karst, these results indicate that the behavior of the catchments of the ‘special interest’ reaches were as aberrant as we hypothesized based on the lack of nutrient response to LULC.

Table 2.2 Characteristics (means) of study stream segments in the four surveys.

<b>Survey</b>	<b>Number of Sites</b>	<b>Gaining (%)</b>	<b>Losing (%)</b>	<b>Stream lengths (m)</b>	<b>LCA (ha)</b>	<b>Canopy LCA (%)</b>	<b>Forested EHA (%)</b>
<b>ALCO</b>	14	71	29	403 (142-1034)	10 (3-26)	91 (40-100)	85 (14-100)
<b>ALSI</b>	14	57	43	293 (105-563)	9 (2-18)	55 (11-90)	38 (6-84)
<b>WACO</b>	11	55	45	537 (149-1469)	22 (4-92)	53 (16-97)	72 (30-100)
<b>WASI</b>	17	41	59	509 (125-1120)	25 (2-69)	29 (4-70)	27 (5-57)

Note: Values computed for ALCO and WACO segments are weighted means; ALSI and WASI values are arithmetic means (value ranges shown in parentheses).

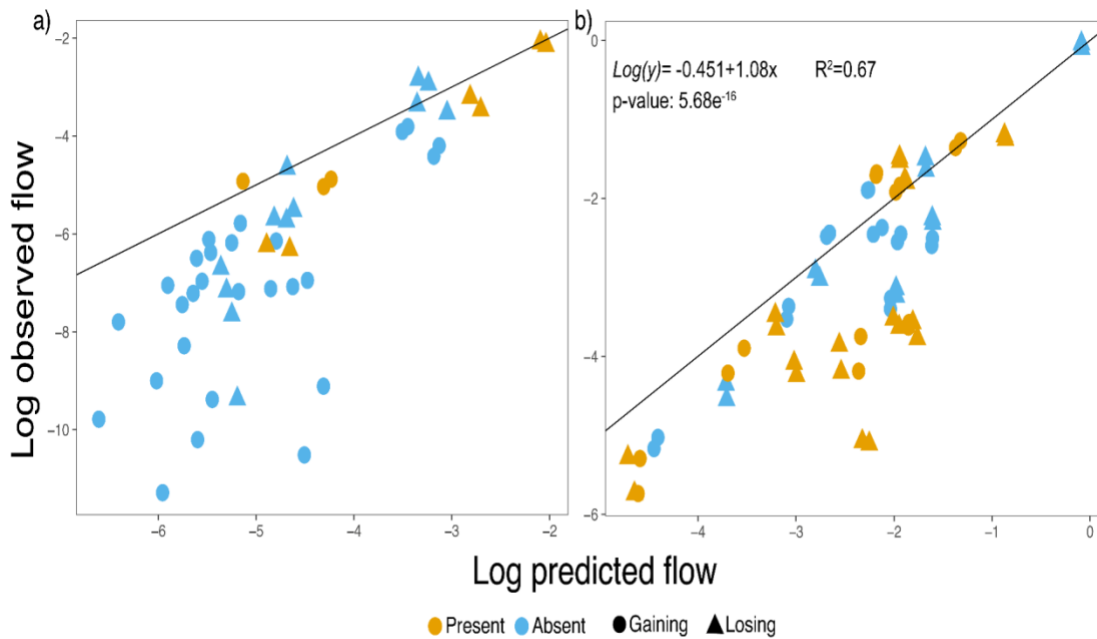


Figure 2.5 Log transformation of raw flow measurements of predicted versus observed stream discharge in (a) ‘randomly selected’ sites (i.e., ALCO and WACO) only and (b) ‘special interest’ sites (i.e., ALSI and WASI) only. p-Value is a result of a simple linear model output where linear regression assumptions are satisfied. (Assumptions were not satisfied for the ‘randomly selected’ sites.) Symbols indicate whether a stream is gaining or losing, and colors represent absence or presence of karst. Solid black lines represent 1:1 relationships between predicted and observed discharges.

Other characteristics of the watershed may also be affecting riparian forests function in the ‘special interest’ sites — sites containing planted buffers through CREP. Therefore, efforts were taken to test some covariates but were not included in the methods section because they did not produce any pivotal results. ANCOVA was used to test if the function of riparian forests on nutrient uptake using concentrations ( $AC$ ) and loads ( $C_{lat}$ ) were affected by stream length, size of forested EHA, and hydrological characteristics that were allotted using the following criteria: observed discharge within 25%, 50%, 75%, within 100%, or greater than 100% of the predicted value. The Kruskal-Wallis test was used to test significance of soil type found using USDA SSURGO

database from the USDA soil taxonomy (included 7 different soil types). From these results, no covariates/variables tested were found to significantly impact riparian forest function.

Our results for modeling the nutrients using two methods (TNC and Gburek & Folmar, 1999) found insignificant p-values between the observed and predicted values for both models. However, Figure 2.6a shows the residual scatterplot using the model from TNC indicating its inaccuracy. Normality, heteroscedasticity, and linearity regression assumptions were violated using the *gvlma* package in R (Peña and Slate 2006) but were met when plotting observed and predicted results for the Gburek & Folmar (1999) model (Fig. 2.6b). The coefficient of determination indicates that approximately 30% of the observed variation can be explained by the Gburek & Folmar (1999) model's input with a few predictions much higher than expected. According to the Akaike information criterion (AIC), used to compare models (Burnham and Anderson 2002), the Gburek & Folmar (1999) model had the most parsimonious fit with a lower AIC value (125.58) compared to the TNC model (388.74). This was expected given the TNC model violated some of the regression assumptions limiting further analysis.

Accounting for the lack of duplicate discharge measurements and grab samples, a paired sample t-test found no significant differences between measured values and those with the incorporated 5 and 10% flow rate error except for the discharge measurements ( $Q_{\text{net lateral}}$  p-value < 0.01) (Fig. 2.7). Incorporating a 5% error in flow measurements changed 44% of the study reaches from net 'losing' to 'gaining' indicating that some reaches were most-likely mislabeled as a 'losing reach' and inaccurately removed from certain analyses. Although not significant, a potential 10% error in field measurements

and water quality data was greatest for  $C_{lat}$  of  $NO_3-N$  and TDN with mean differences of 16.8 and 12.9 mg/L, respectively.

## ***2.5 Discussion***

Our study was designed to evaluate whether the hydrogeomorphological characteristics of a catchment, especially in the R&V physiographic province, influences how stream water quality responds to the presence and planting of riparian forests. We hypothesized that if the EHA is accurately defined along the reaches where the interactions between ground and surface waters are prevalent, then nutrient retention will be positively correlated with percent forested EHA. Overall, our results were inconclusive, but provided some clear empirical evidence that mature forested riparian areas are more effective in reducing nutrient concentrations in streams than recently planted buffers, even though significant differences were not detected between the two site categories.

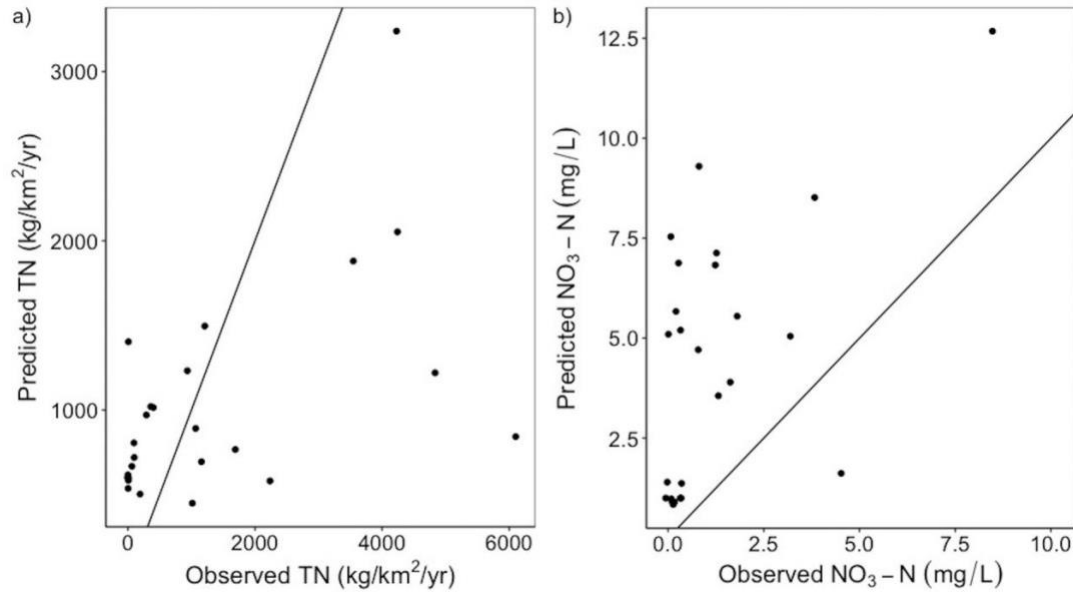


Figure 2.6 (a) Comparison of observed and predicted TN loads in kg/km<sup>2</sup>/yr using the Chesapeake Bay model (CBP) and (b) observed and predicted NO<sub>3</sub>-N concentrations in mg/L using Gburek & Folmar (1999) model. Lines represent a 1:1 perfect theoretical relationship between the observed and predicted values. The CBP model shows a mix of under and over predictions and Gburek & Folmar (1999) indicates majority of over predictions.

The study produced more examples of  $C_{lat}$  of N and P decreasing as a response to increased forested EHA and canopy cover compared to  $\Delta C$ , where only P concentrations declined (Table 2.1). While the exact processes occurring within these study reaches are uncertain, the reduction of P based on the  $\Delta C$  results may be a consequence of the binding capacity of sediments along the bank (Vought et al. 1994). Even along losing streams, this process allows P to precipitate as calcium phosphate or Fe(II) phosphate in alkaline soils. However, P may be released from stream bank erosion, which could be stabilized by riparian vegetation (Hoffmann et al. 2009, Thompson and McFarland 2010). Furthermore, the binding capacity may limit P precipitation by the availability of Ca compounds and the presence of ions, such as carbonate, where the formation of calcium carbonate reduces free Ca concentrations (Song et al. 2002). The reductions of both N

and P from the  $C_{lat}$  analysis indicate assimilative and dissimilative processes (Ruehl et al. 2007), which both require the presence of vegetation for either direct plant uptake or to serve as a carbon source for denitrification (Gift et al. 2010, Burger et al. 2010, Hill 2019). Nutrient removal from assimilation is only a temporary reduction where it can be released back into the environment via degradation and mineralization (Ruehl et al. 2007). It is unclear which processes are responsible for the nutrient reductions, but evidence suggests it is at least associated with a greater density of forests in the catchment and riparian area.

While there is similarity between our findings and other studies that found discharge of N and P decrease with greater proportions of canopy and forested riparian area within a catchment (Dillon and Kirchner 1975, Hill 1978, Neill 1989, Rekolainen 1989, Mason et al. 1990, Jordan et al. 1997a), other studies performed in the R&V did not find strong correlations between nutrients and land use (Schomberg et al. 2005, Weller et al. 2011). Deeper groundwater flowpaths in the R&V can extend the residence time of excess nutrients and disrupt nutrient removal potential via riparian forests (Böhlke and Denver 1995, Lowrance et al. 1997, Puckett et al. 2002). Thus, our results indicate surface/ground water connectivity likely exists within watersheds containing gaining reaches where the groundwater intersects with riparian vegetation before discharging into surface waters.

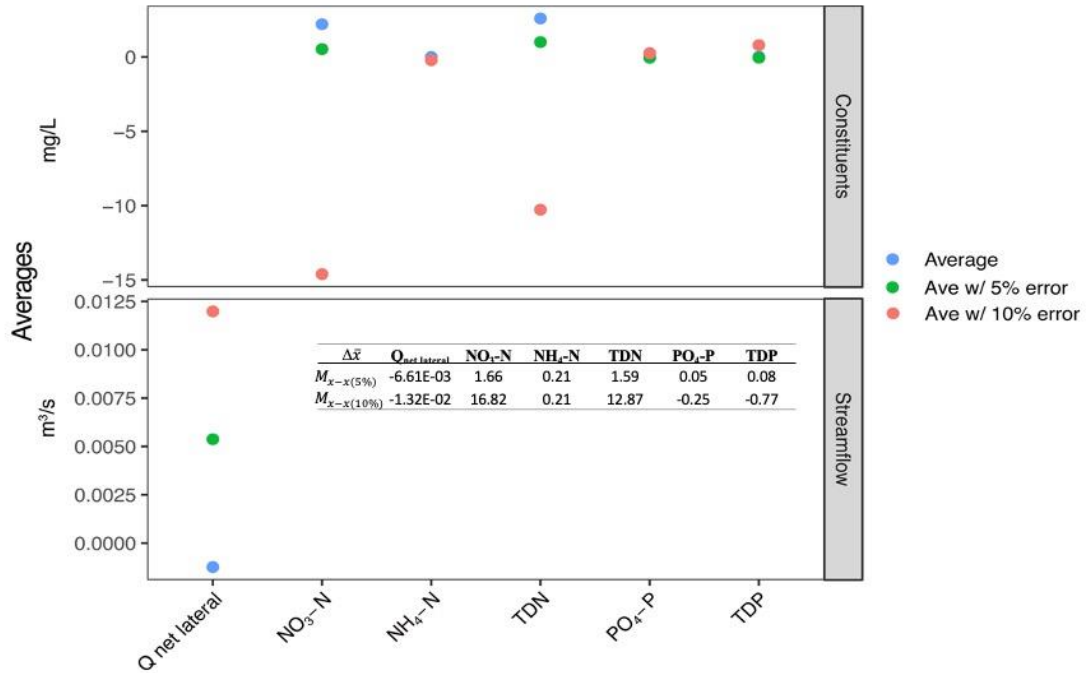


Figure 2.7 Averages of calculated net lateral discharge ( $Q_{net\ lat}$ ) and nutrient concentrations of net groundwater lateral inflow using measured results (solid blue circles) and an incorporation of  $\pm$  5% (solid green circles) and 10% (solid red circles) error of uncertainty. The table shows the differences between the averages. Using a paired t-test, the mean difference between the average discharge rate with and without the 5% and 10% incorporated errors were the only results found to be significantly different from zero (p-value < 0.01).

Newly planted buffers within the ‘special interest’ sites do not appear to remove/retain nutrients as well as the mature forests within the ‘randomly selected’ sites. We surmise several possible reasons, such as: (1) newly planted riparian buffers were not yet adequately established and lacked the capability of reducing nutrient pollution or serving as a significant source of carbon that supports biological processes (Burger et al., 2010); (2) ‘special interest’ sites had less percent canopy (i.e., more percent agriculture) within the LCA compared to the ‘randomly selected’ sites (Table 2.2), potentially generating higher nutrient levels in subsurface waters; and (3) supposing nutrient uptakes rates were the same within the forested EHA across all sites, the nutrient loads would still



be higher in ‘special interest’ sites if the groundwater upland from the riparian area had higher nutrient loads. Based on our results, it is premature to conclude whether riparian forests are ineffective in this region, but evidence thus far does not prove their success. However, the significant negative correlations between nutrients and FEHA when combining all sites indicates that the ‘special interest’ sites will eventually reduce nutrients to the same degree as the ‘random sites’ — a conclusion further supported by finding no significant differences between the planted or natural forest buffers using ANCOVA. However, it may require several years before showing significant improvements in water quality, especially in karst regions where it can take at least a decade depending on the water source and residence time (Lindsey et al. 2003).

The stipulations of CREP may be inhibiting riparian buffer potential to reduce nutrients in the R&V. CREP was established in Maryland in 1997 (USDA and FSA 2018) where the majority of the riparian forests in Allegany and Washington Counties were established before 2006 (Fig. 2.8) (Winters 2018c). Landowners who participate in CREP sign a 10- or 15-year contract, which is less than the recommended time period for riparian forests to become well enough established (Mander et al. 1997, Newbold et al. 2010). However, in the next few years, about 10% – 30% of existing buffers will expire under CREP (Maryland State Task Force 2017). According to the STATSGO hydric soil data layer, soil classification based on runoff potential, infiltration rate, water transmission, and prime farmland was not a significant factor explaining the current landuse/ landcover of the riparian area (i.e., natural forest, CREP plantings, or cropland) based on anecdotal observation. The soils throughout these subwatersheds are very heterogenous and landowner decisions to maintain or plant a riparian buffer does not

seem to be controlled by soil characteristics. Therefore, once CREP contracts expire, land could be converted to agriculture unless restricted by steep slopes, which seems to be a factor. We suggest longer contracts and higher incentives to encourage landowners to preserve newly planted riparian forests so that they have enough time to mature and become functional.

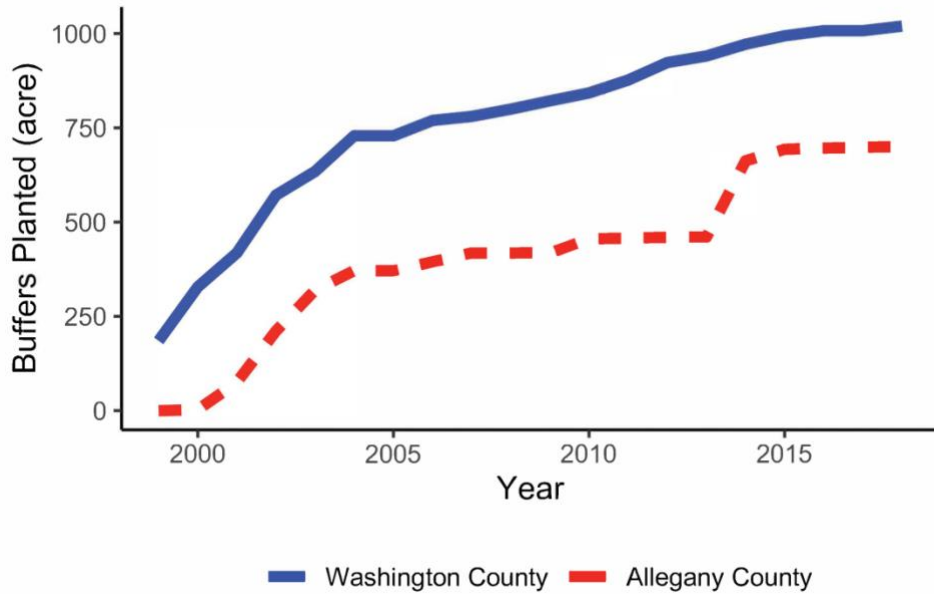


Figure 2.8 Line graph showing the cumulative sum of riparian forest buffers planted over time in Allegany County (dashed red line) and Washington County (solid blue line). Data provided by Maryland Department of Natural Resources (2019).

Better management may also be required for buffers to successfully become established in this region. One study evaluating the establishment of one- to five-year-old riparian buffer plantings through CREP found more than 90% of planted trees survived in the Coastal Plain (CP) and Piedmont of the CBW, but only 68% of planted trees survived in the R&V. Natural regeneration density (stems ha<sup>-1</sup>) averaged 8,540 in CP and 2,782 in the Piedmont, but only 380 in the R&V. Furthermore, 44% of the natural regeneration in the R&V was by two exotic invasive species: *Ailanthus altissima* (tree of heaven) and

*Elaeagnus umbellata* (autumn olive). The low success rate in the R&V was attributed to management (mowing, grazing, disking, etc.), invasive species, and isolation from healthy forest communities (i.e., seed sources from native species) (Bradburn et al. 2010). Therefore, better management, more tree plantings, protective fencing, control of exotic species, and a longer contract period with landowners may be required before seeing stronger evidence of nutrient retention from riparian buffers.

While we found some significant results indicating that a forested EHA and catchment can improve stream water quality within the R&V, our study design hinders our ability to derive a clear conclusion. In particular: 1) the sample size was relatively small; 2) some unknown covariates not sampled could have affected the results; 3) there was no replication (only a single, instantaneous measurement and sample of each reach was taken); 4) ‘special interest’ reaches were not randomly chosen and could not be included in some of the analyses; 5) pre-planting riparian buffer data were not available; 6) losing reaches had to be removed for  $C_{lat}$  analyses; and 7) some losing reaches may have been incorrectly classified due to sampling error.

Another caveat was the neglect of in-stream processing in our models to make inferences about LULC in the watershed. Where nutrient concentrations declined, we considered those changes to result from hydrologic dilution. Other studies have found declines of  $\text{NO}_3^-$  concentrations that could not be predicted by land use—thus differences were attributed to unmeasured in-stream processing (Aber et al. 2002, Bernhardt et al. 2005a). In shallow, slow-moving streams, nitrate removal rates ranged from 0.4 to 6.5% per meter with an average of 1.5% per m (Bernhardt and Likens 2002). Therefore, we speculate that some of the nutrient losses in these reaches were due to biological in-

stream processes and not exclusively because of riparian forest presence. In future work, efforts to execute a more comprehensive comparison between sites with planted and naturally forested riparian areas should include surveys of tree characteristics (e.g., growth, species, age, and density); water samples collected from the upland groundwater; and direct measurements of in-stream processing.

Other than nutrient pollution mitigation, riparian buffers produce other benefits. They enhance habitats in riparian and aquatic ecosystems (Kuglerová et al. 2014), sustain riparian soil for erosion control (Kreutzweiser and Capell 2001), and serve as a carbon source that supports food webs (Kuglerová et al. 2014). These benefits support the installation and conservation of riparian buffers regardless of whether they have a strong potential to remove nutrients. However, our study suggests that once buffers are established and mature, they have a greater potential of removing nutrients if installed in locations conducive to nutrient uptake. This will rely on topography, hydrologic flowpath, and assurance that groundwater traverses through the riparian buffer. According to Weller et al. (2011), the Appalachian Mountains have the most buffer “gaps” (71%), providing more opportunities for nutrient rich groundwater to pass through unbuffered areas. Therefore, simply filling riparian forests gaps could be a useful management approach for locations where continuous buffers are lacking, since evaluating the hydrologic flowpath of each catchment would be a challenging and tedious task. Furthermore, regardless of the buffer’s function, its presence automatically lessens the potential for nutrient runoff by reducing the area of fertilized cropland.

Models used to predict N loads/ concentration and groundwater discharge were subpar but factors influencing their performance is unclear. Models used to predict

nutrient concentrations and loads based on LULC data (TNC & Gburek & Folmar (1999)) showed some correlation but were far off from an optimal fit (i.e., 1:1 line). Gburek & Folmar (1999) was the better model according to the AIC and explained 30% of the observed variation. Lindsey *et al.* (2001) used the same model with adjusted variables for a catchment within the R&V and found it successfully predicted nutrient concentrations at a larger scale, but it was within the same watershed as Gburek & Folmar (1999). We suspect deriving a better set of model coefficients for our watersheds would provide little improvement due to several caveats: (1) the model assumes that nutrient concentrations in shallow groundwater are the primary effect on surface water quality; (2) the model coefficients were calibrated to land use and hydrogeologic conditions to a specific watershed; and (3) the model assumes equivalent surface and subsurface watershed boundaries. Discharge using catchment area and data from USGS gauging stations revealed that discharge did not scale directly with watershed area for most reaches. About 55% of reaches had a greater than 100% difference between the measured and predicted discharge rate, most-likely affecting nutrient loads. This was a mix between sites with and without karst containing both losing and gaining reaches. We suspect karst had some influence on the models, but no significant correlations were found between karst presence and the reaches' hydrological characteristics.

Although there were no correlations between losing reaches and karst, we assume some of these sites were mislabeled, which affected our results. We used the most recent karst map from 2014 to find where karst overlays within our sites, but comparing this with a map published in 1984, some sites classified differently. As previously noted, the US Karst Maps (Weary and Doctor 2014) are created based on karst potential, which may

lack the high-resolution capability needed to assess reaches throughout this landscape. Lack of correlation between losing reaches, or those containing springs, based on landforms that can be detected using remote sensing data makes it difficult to determine the hydrological characteristics of each reach without measuring the downstream and upstream flowrates. Furthermore, we also suspect that when measuring one particular location of a stream provides only a snapshot of the flows in and out from an entire channel, especially in lower order streams. In higher order streams, this balance seems to be maintained, based on the improvement of the USGS model after removing streams with low discharge rates and a similar study that found smaller basins containing net losing reaches had lost surface water to a parallel subsurface flowpath that then re-emerged with surface waters further downstream (Lindsey et al. 2001). Identifying karst and other geological features are difficult as groundwater divides may change, depending on where the groundwater is recharged, and the channels in bedrock aquifers most-likely are not following surface topography (White 2002, Becker et al. 2004). Future directions of research to advance our understanding of changes along a stream continuum in karstic landscapes should include following a stream throughout its entire mainstem (from headwaters to its final discharge into a larger body of water) while using a steady-state reach mass balance model that incorporates incoming tributaries and springs.

## ***2.6 Conclusion***

Forest cover affects nutrient loads in streams, although the mechanism (fewer nutrient inputs or better nutrient sinks or both) can't be determined. Evidence supporting the effectiveness of planted riparian forests was equivocal, but we found evidence that older, established forests have the ability to reduce nutrients in groundwater suggesting

that emphasis be placed on preserving already forested lands. One can speculate that as planted forests grow older, they will eventually perform as did randomly sampled mature forests, but it can take a long time for planted buffers to become functional, which may exceed the CREP contract period. The R&V presents challenges identifying the most effective sites for riparian forest buffers due to flowpaths that bypass riparian zones, but nevertheless we suspect riparian buffers to be planted because of their importance as a BMP in other geographies and the natural decline of nutrients from the watershed by replacing fertilized farmland. Nevertheless, riparian buffers will be most effective if implemented where streams are gaining. They should be managed well to develop canopy cover, and co-benefits should be recognized whenever possible (e.g., bank stabilization, maintain stream temperature, forest products, terrestrial wildlife habitat, etc.).

## ***2.7 Acknowledgements***

We thank the Maryland Department of Natural Resources for allowing us access to their Conservation Reserve Enhancement Program files to determine location of planted buffers and for their assistance with the study. We thank Nathan Reinhart for his assistance in digitizing all of the planted CREP riparian buffers in ArcGIS and Robert Sabo for his assistance in site selection. The authors would also like to thank Eric Davidson and Thomas Fisher for their editorial reviews. This research was supported by a grant from the National Fish and Wildlife Foundation to Maryland DNR.

## Chapter 3: Assessing riparian hydrologic pathways as controls on forested buffer function in four subwatersheds in western Maryland

### *3.1 Abstract*

Several studies support the use of riparian forest buffers as a best management practice in mitigating excess nutrients in groundwater from agricultural fields. However, of the few studies performed in the Ridge and Valley (R&V) physiographic province of the Chesapeake Bay watershed, most results show uncertainties and inconsistencies due to karst landscapes. To assess this ambiguity of riparian buffer function in this province, we performed synoptic stream chemistry baseflow surveys within four subwatersheds in the R&V in western Maryland three times (two spring and one fall season). Streamwater “grab” samples were collected and tested for nutrients (N & P), ions, and isotopes. Stream water discharge measurements were taken along the mainstem and at the confluences of tributaries and karst springs. We estimated lateral groundwater inputs using a steady-state reach mass balance model, neglecting rates of in-stream nutrient processing. We found that several of the mainstem reaches were either losing, or largely gaining from tributaries and karst springs, rather than groundwater. Gaining reaches from net lateral inflow showed negative correlations between forested local catchment and riparian areas and estimated groundwater nutrient concentrations. However, we found little evidence that planted buffers reduce nutrient pollution. This suggests that within karst areas, mature riparian forests may be more effective at reducing nutrients than newly established buffers. In an effort to explain nutrient discharge during baseflow conditions with karst topography, we developed two models: an “actual flow model” that uses measured flow, and a “base model” that uses catchment area. We found the “actual



flow model” to be the better predictor of nutrient concentrations. This result demonstrates the hydrogeological complexity of karst landscapes where discharge is not necessarily a simple function of catchment area or land use.

### ***3.2 Introduction***

The Chesapeake Bay (CB) is the largest estuary in the United States and is an important commercial and recreational resource ((NRC et al. 2011). Its watershed expands over six states (Delaware, Maryland, New York, Pennsylvania, Virginia, and West Virginia) and the District of Columbia (NRC et al. 2011, Lee et al. 2016). Human activities within its watershed have periled CB’s aquatic ecosystem, particularly with total phosphorus (P) and nitrogen (N) from agriculture. As a result, the Bay states came together as Bay jurisdictions to implement initiatives that would reduce pollution to appropriate levels, ultimately restoring the CB (NRC et al. 2011).

One initiative is restoring forests along riparian areas. Studies show riparian buffers can reduce nutrients from subsurface and surface runoff before discharging into receiving waters (Jordan et al. 1993, Lowrance et al. 1997). This finding led to a state and federal partnership program, the Conservation Reserve Enhancement Program (CREP), first implemented in Maryland in 1997. The program derived from the Conservation Reserve Program (CRP) and focuses on priorities set by the state with emphasis on environmental concerns on a multi-farm, landscape scale (Allen 2005). Farmland owners can enroll a parcel of their land if it meets a certain criterion (e.g., adjacent to a body of water and environmentally sensitive). Once approved, the land is taken out of crop production and dedicated to a riparian buffer for a 10- to 15-year contract period. In

return, farmland owners receive pecuniary incentives and installation support from local soil conservation districts (Allen 2005, Oberg and Orlando 2014).

Maryland intends to enroll 40,500 ha of eligible land into CREP to reduce sediment and nutrient loads within the CB and its tributaries. If this target is achieved, models estimate an annual reduction of 5.2 million kilograms of N, 0.5 million kilograms of P, and 200,000 tons of sediment (Oberg and Orlando 2014). However, the accuracy of the models depends on several factors, such as hydrological interactions between surface and adjoining groundwater and hyporheic environments (e.g., soil type; local hydrogeological conditions; groundwater residence time; water table depth; and topography/slope) and characteristics of the buffers themselves (e.g., species planted, survival rate, density, age, etc.) (Böhlke and Denver 1995, Hill 1996, Lowrance et al. 1997, Gold et al. 1998, 2001, Schoonover and Williard 2003). These controls were evaluated within all physiological provinces of the CB watershed, including the Coastal Plain, Piedmont, Ridge and Valley (R&V), and Appalachian Plateau, with only a few studies performed in the two latter provinces, which make up 60% of the CB watershed (Lowrance et al. 1997) and contain the two largest tributaries (i.e., the Susquehanna and the Potomac Rivers) (Lang and Grason 1982, Miller et al. 1997, Piechnik et al. 2012). Of those few studies, they concluded that uncertainty and variability in nutrient reductions because of the heterogeneity of the landscape from the karst-terrain that affects near-stream hydrology (Schnabel et al. 1997, Weller et al. 2011, Husic et al. 2019). Karst landscapes contain fractures in bedrock that disrupt subsurface lateral flows through the riparian area (Miller et al. 1997, Husic et al. 2019), which hinders the potential for nutrient mitigation via vegetation uptake and microbial processes (Miller et al. 1997).

Groundwater traversing through these bedrock fractures most often follow deep groundwater flowpaths that delay the discharge of water from karst springs into surface waters by many years (Kavousi and Raeisi 2015). Losing reaches are also prevalent where surface waters recharge groundwater. Thus, the hydrogeomorphology of the landscape can affect buffer function and lead to inaccurate statistical models that managers rely on to reach restoration goals.

Thus, the objective of this study was threefold. By conducting a synoptic survey of four subwatersheds from headwaters to the final outlet within the R&V under seasonal baseflow conditions, first, we examined the direction and magnitude of lateral groundwater discharge and the dominant sources of the mainstem. We hypothesized our study sites along the mainstem would be a mix between losing and gaining reaches, with at least half of the gaining reaches dominated by tributary waters or karst springs, rather than lateral groundwater discharge. Second, we explored if any correlations exist between land use/land cover (LULC) (including planted riparian forest buffers) with nutrient loads in lateral groundwater discharge. We predicted direction and magnitude of lateral groundwater discharge to the mainstem to be the primary control of the interactions between ground- and surface waters, thus affecting nutrient mitigation potential. We also considered the dominant sources of water to the mainstem (i.e., diffuse lateral groundwater, karst springs, and tributaries) as controlling nutrient concentrations and loads, rather than LULC. Third, we developed two statistical models — one that uses measured flow (“actual flow model”) and another that uses catchment area (“base model”) — to explain nutrient concentrations in karst regions. Because of the complex

hydrogeomorphology of the R&V, we suspected the “actual flow model” would be superior.

### **3.3 Methods**

#### **3.3.1 Study region**

The Ridge & Valley’s (R&V) unique landscape contains continuous oscillations between northeast-trending ridges and valleys. The ridges contain acidic soils from the chemical weathering of sandstone and chert, and the valley beds contain weaker shale and desultory karst terrain underlain by limestone and dolostone (White 2002). Within the valley beds are flowing streams, accompanied by intermittent springs throughout the shale and siltstone terrane where flow ceases during drought (Otton and Hilleary 1985). The valleys contain thick, fertile soils from the breakdown of shale and limestone (Chowns 2018), with relatively shallow depths (<1.5 m) that just covers the underlying bedrock (Gburek and Folmar 1999b). Generally, forests dominate the upland portion of the basin and croplands dominate the valleys (Gburek and Folmar 1999b).

#### **3.3.2 Study design**

We investigated the function of riparian forest buffers using four subwatersheds of the Potomac River in the R&V physiographic province within the state of Maryland (Figure 3.1A). One is located in Town Creek watershed in Allegany County and the other three are in Antietam Creek watershed in Washington County. The subwatershed within Town Creek includes Murleys Branch (MB; area=32 km<sup>2</sup>) (Fig. 3.1B) and has a land surface elevation of 254 m (Maplogs 2019) with precipitation averaging approximately 949 mm y<sup>-1</sup> (NOAA 2019). The three selected subwatersheds located in Antietam Creek includes: Little Antietam Creek North (LACN; area= 64 km<sup>2</sup>) (Fig. 3.1C); Beaver Creek

(BC; area =87 km<sup>2</sup>) (Fig. 3.1D) and Little Antietam Creek South (LACS; area= 83 km<sup>2</sup>) (Fig. 3.1E). Land surface elevation is approximately 95 m (National Water Quality Monitoring Council 2019), with precipitation averaging 1077 mm y<sup>-1</sup> (NOAA 2019). Within the riparian area, soils varied from low porosity, high erodibility to high porosity, low erodibility (Soil Survey Staff and Natural Resources Conservation Service 2017). Each of the four subwatersheds also includes a considerable number of CREP participants.

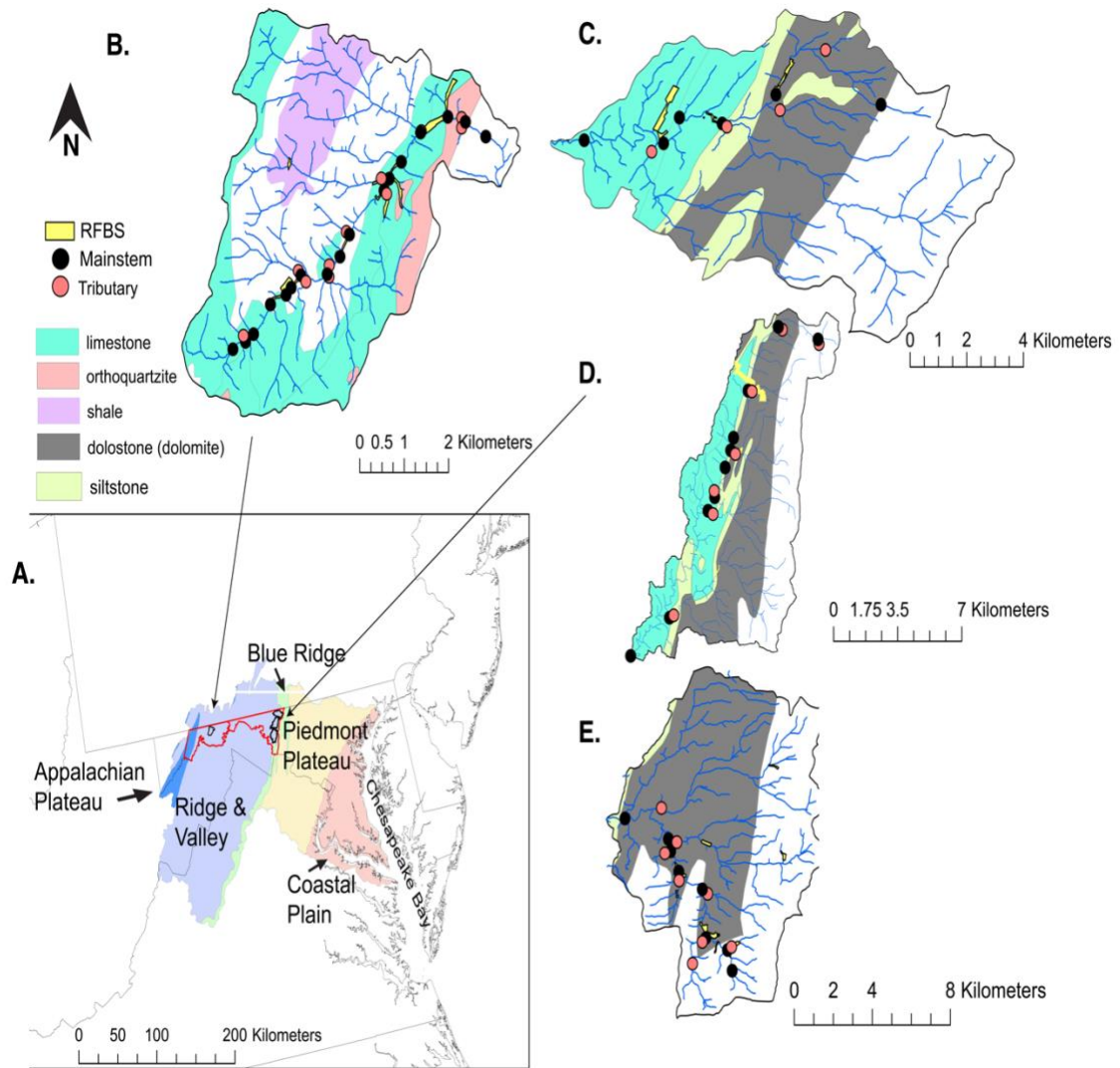


Figure 3.1 (A) Map of study sites in western Maryland (Allegany and Washington Counties outlined in red) showing the physiographic geological provinces within the Potomac River watershed of the Chesapeake Bay. Subwatersheds show location of karst topography for (B) Murleys Branch (MB), (C) Little Antietam Creek North (LACN), (D) Beaver Creek (BC), and (E) Little Antietam Creek South (LACS). Areas inferred to have no karst topography are white. MB is in Allegany County, Town Creek watershed and the others are in Washington County, Antietam Creek watershed. The subwatersheds of Antietam Creek are adjacent to one another – going north to south: LACN, BC, and LACS (as shown in this figure).

### 3.3.3 Field study design

Within each of the four subwatersheds, we conducted three comprehensive, longitudinal, synoptic stream surveys under baseflow conditions. Two surveys were

conducted during the spring season (one in 2016 and the other in 2017) and the third survey was conducted during the fall season (2016). We ensured consistent hydroclimatological conditions for each survey by sampling each subwatershed in its entirety on the same day and avoided stormflow conditions by referencing hydrographs of USGS gauged basins within Allegany and Washington Counties (i.e., Town Creek and Antietam Creek USGS gauges, respectively). We identified sampling locations (i.e., “stations”) using a high-resolution stream map to locate springs and tributaries along the mainstems. Once located, we made “instantaneous” wading stream discharge measurements and collected “grab” streamwater samples for water quality analysis from (1) the mainstem, just above the confluence with a tributary or major spring; and (2) near the downstream end of each tributary or spring discharging into the mainstem, unless we were able to find a more convenient access point (i.e., at a road crossing or other locations where we could get permission to access the stream from tenants or property owners). The synoptic survey portion of the study included a total of 74 stations (31 in MB; 17 in BC; 10 in LACN; and 16 in LACS).

### **3.3.4 Field and laboratory methods**

We measured velocity at 0.6 times the water depth from the water surface at 10 to 30 regularly spaced intervals along a suspended tagline using a Marsh-McBirney digital electromagnetic current meter attached to a top-setting wading rod. Total instantaneous discharge was computed using the mid-section method. We collected grab samples in 1L polyethylene cubitainers that were immediately placed on ice in a cooler and transported to our analytical laboratory where they were filtered (0.45  $\mu\text{m}$ ), aliquoted, and stored in 4 degrees Celsius until analyzed without exceeding holding times. Holding times followed

standard EPA (1999) and APHA (1998) methods (Chanlett 1947, O'Dell 1996, Kline 2013). We analyzed the grab samples for nutrients (TDN, TDP, PO<sub>4</sub>-P, NH<sub>4</sub>-N, NO<sub>2</sub>-N, and NO<sub>3</sub>-N) using a Lachat QuikChem 8000 flow injection analyzer; major ions (chloride: Cl<sup>-</sup>; bromide: Br<sup>-</sup>; sulfate: SO<sub>4</sub><sup>2-</sup>; calcium Ca<sup>2+</sup>; magnesium: Mg<sup>2+</sup>; sodium: Na<sup>+</sup>; and potassium: K<sup>+</sup>) by ion chromatography (anions) and atomic absorption/emission spectroscopy (cations); specific conductance (meter); acid neutralizing capacity (ANC) by automated acidimetric Gran titration; dissolved organic carbon (DOC) by UV-assisted persulfate digestion; and dissolved silica (SiO<sub>2</sub>) for fall (2016) and spring (2017) samples only using an inductively coupled plasma mass spectrometry (ICP-MS). Laboratory duplicates, blanks, calibration checks, and control samples were analyzed to ensure quality of the analytical results.

Major ion concentrations were used to test our methodology for identifying losing and gaining reaches by employing a steady-state reach mass balance model for less biologically reactive constituents. Ions, along with conductivity and SiO<sub>2</sub>, were also used to show composition changes from station to station along the mainstem with influence from tributaries and springs. Relationships between NO<sub>3</sub>-N and Cl<sup>-</sup>/SO<sub>4</sub><sup>2-</sup> were investigated to determine nitrate pollution sources. Studies have found positive correlations between NO<sub>3</sub>-N and Cl<sup>-</sup> with a correlation coefficient greater than 0.35 indicate contamination of water from septic tanks and sewage (Chen et al. 2017, Adimalla 2020) and positive relationships between NO<sub>3</sub>-N and SO<sub>4</sub><sup>2-</sup> generally indicate fertilizer (Esmacili et al. 2014, Chen et al. 2017). The Shapiro-Wilk test indicated that parameters were not normally distributed with p-values less than 0.05; thus Spearman's Rank correlation coefficient (Siegel and Castellan Jr. 1988) was used to determine



correlations. Each season (i.e., spring and fall 2016, and spring 2017) was analyzed separately using all sites, mainstem sites only, karst springs only, tributaries only, and sites from individual subwatersheds.

We added a nitrate isotope analysis ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$ ) for one sampling period for each of the sites (i.e., spring 2017 samples for MB and spring 2016 samples for LACN, BC, and LACS) to ascertain if denitrification or biological processing are occurring within the subwatersheds. Methods followed the bacterial denitrifier procedure defined in Sigman *et al.* (2001) and Casciotti *et al.* (2002) by measuring nitrous oxide gas produced from the denitrification process. Thermo Delta V+ Isotope Ratio Mass Spectrometer was used to measure the isotopes and USGS 32, 34, and 35 standards were used to normalize the data. Within-run precisions for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  were  $\pm 0.2$  ‰ and  $\pm 0.4$  ‰, respectively, and the between-run precisions were  $\pm 0.3$  ‰ and  $\pm 0.9$  ‰.

### **3.3.5 Defining catchment area and land-use**

We marked study sites in the field using a Garmin eTrex 20 Global Positioning System (GPS) and uploaded them into ArcGIS as waypoints. Figure 3.1B-E shows the study sites in each subwatershed, along with KMLUS Karst Map from U.S. Geological Survey to indicate the location of underlain soluble rocks conducive to karst formations (Weary and Doctor, 2014). Using these waypoints, along with a 10-meter digital elevation model (DEM), total contributing areas (TCA) of each reach was delineated using the Archedro tools and a flow accumulation raster where preprocessing was performed with the TauDEM software package (Tarboton *et al.* 2009). The difference between two drainage basins of the upstream and downstream outlet (TCA's) was used to calculate the local contributing area (LCA) of each site. The eco-hydrologically active

(EHA) area (or riparian region) for each LCA of each reach was defined with the help of our partners from The Nature Conservancy (TNC). Detailed information of the methodology can be found in Chapter 2.

Land use properties (e.g., canopy cover, agriculture, and biomass) were obtained from maps acquired from the Department of Geological Sciences at UMD. Land use was calculated in TauDEM using the FAC tool with each of the LULC rasters used as the optional weight (Tarboton et al. 2009). USDA Cropscape Data layer from 2016 (CDL 2018) was used to define specific agricultural land uses in the LCAs. Although sampling occurred in both 2016 and 2017, results of a Welch Two Sample t-test indicated that land use stayed fairly consistent between these two years; therefore, only the 2016 data are shown in Figure 3.2.

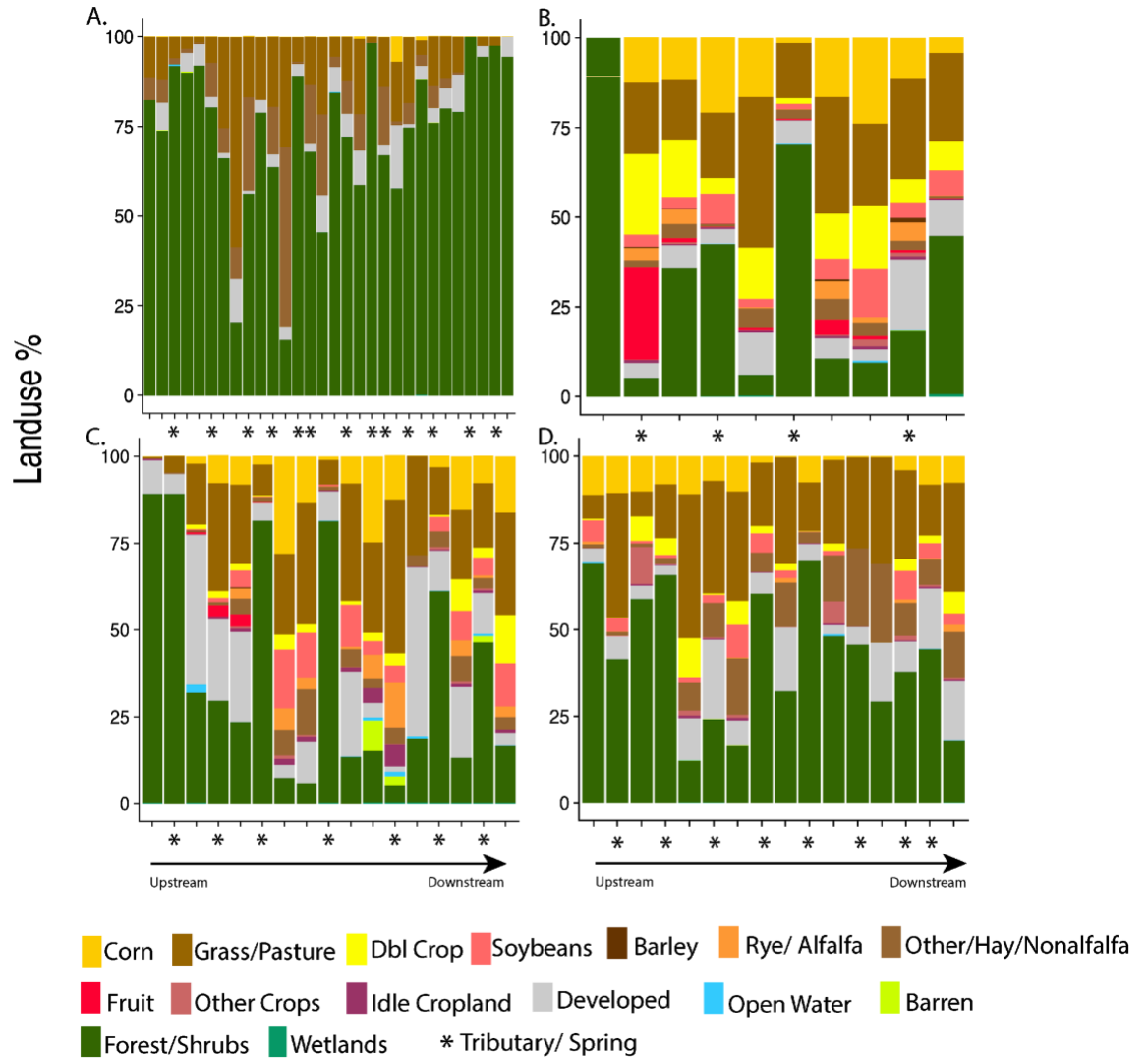


Figure 3.2 Bar chart showing the land use of each local contributing area of each site for the four subwatersheds: (A) Murleys Branch, (B) Little Antietam Creek North, (C) Beaver Creek, and (D) Little Antietam Creek South. Sites are arranged from left to right, indicating downstream to upstream. Tributaries are highlighted by the asterisk. Land use data is from Cropscape Data Layer using year 2016 (USDA, 2018).

The Conservation Reserve Enhancement Program (CREP) documents, provided by the Department of Natural Resources (DNR), allowed us to digitize and quantify the number of program participants within our subwatersheds of interest. Table 3.1 provides this information, along with an overview of riparian forest buffers in each subwatershed,

including: percentage of the TCA dedicated to the riparian buffers, percentage of streams buffered within the entire subwatershed, range and average year riparian forest buffers were planted, and range and average of canopy cover for each riparian forest buffer (statistics of riparian forest buffers were found using ‘Zonal Statistics as Table’ tool in ArcGIS). A total of 24 farmers were identified as participating in CREP projects within these subwatersheds.

Table 3.1 Riparian Forest Buffer (RFB) data for each subwatershed (Murleys Branch – MB; Beaver Creek – BC; Little Antietam Creek North – LACN; and Little Antietam Creek South – LACS).

<b>Sub-watershed</b>	<b>Total # of CREP Participants</b>	<b>% RFB per TCA</b>	<b>% of stream buffered</b>	<b>Range of years RFB were planted</b>	<b>Ave Year RFB were planted</b>	<b>Range of % Canopy Cover within each RFB</b>	<b>Ave % of Canopy Cover in RFB</b>
<b>MB</b>	5	1	11	2000-2007	2002	9-50	35
<b>LACN</b>	4	0.6	5.5	1999-2004	2002	16-66	39
<b>BC</b>	5	1	5	2000-2003	2001	29-85	49
<b>LACS</b>	10	0.85	9	1999-2003	2001	20-87	47

For qualitative, analysis purposes, we acquired ESRI® data, when possible, to ascertain the geology and soil type of each subwatershed using ArcGIS. Complete description geology maps were available for the Antietam Creek sites (i.e., LACN, BC, and LACS); however, geology maps do not exist for the MB subwatershed because of its remote location. Myersville & Smithsburg Quadrangle and Keedysville & Shepherdstown Quadrangle were acquired from the Maryland Geological Survey (MGS) to gather qualitative data on LACN, BC, and LACS, respectively (Brezinski 2009, Brezinski and Fauth 2009). Both geologic maps are 7.5-minute quadrangle maps

(1:24,000 scale) (Maryland Geological Survey, 2018). ESRI® data from Soil Survey Geographic (SSURGO) by the United States Department of Agriculture's Natural Resources Conservation Service (USDA/NRCS) was downloaded and used for all sites but was again unavailable for MB subwatershed. A soil report was instead developed through their website (Soil Survey Staff and Natural Resources Conservation Service, 2017) for MB, but unfortunately, there was no substitute for geological data.

### **3.3.6 Hydrological modeling**

Net (instantaneous) lateral groundwater discharge (to each reach  $i$ :  $Q_{lat(i)}$ ) was computed as the difference between the discharge measured at the downstream site ( $Q_{D(i)}$ ) and the discharge measured at the upstream node of reach  $i$  ( $Q_{u(i)}$ ) plus the discharge (if any) from the corresponding tributaries ( $Q_{T(i)}$ ) or springs ( $Q_{S(i)}$ ). Computed negative values of  $Q_{lat(i)}$  were thus indicative of a losing reach; however, if the reach was found to be gaining after incorporating 5% error in the flow discharge calculation, the stream was relabeled as “indefinite” to compensate for the possibility of experimental error in the field discharge measurements. A 5% error was used to account for possible measurement error since the volumetric flow rates were only measured once due to time and accessibility. Five percent was used because most discharge measurements have indicated a 3 to 6 percent standard error under conditions similar to our study (no shortcuts taken, use of calibrated equipment, measurements taken in a stable streambed, etc.) and we used the mid-section method where computational errors are usually small (Sauer et al. 1992).

Measured discharge was compared to the modeled daily discharge that was calculated using the closest United States Geological Survey (USGS) gauging station.

USGS 01609000 Town Creek near Oldtown, MD was used to model discharge in MB and USGS 01619500 Antietam Creek near Sharpsburg, MD was used to model discharge in LACN, BC, and LACS. Mean daily discharge was assumed to be directly proportional to the drainage area following Eq. (1):

$$Q_n = \frac{Q_{USGS}}{TCA_{USGA}} * TCA_n, \quad (1)$$

where  $Q_{USGS}$  is the mean daily discharge taken from the appropriate USGS gauging station (U.S. Geological Survey 2019) on the specific dates flow rates were measured,  $TCA_{USGS}$  connotes the total contributing area for the outlet of the USGS gauging station, and  $TCA_n$  is the total contributing area for each specific field station along the mainstems. Since we sampled during baseflow conditions, we assumed all incoming water was lateral groundwater inflow (Hornberger et al. 1998). We compared the predicted values with our field data to learn where lateral groundwater discharge was not correlated with catchment size. Large differences between observed and predicted discharge insinuated that the catchment had a complex hydrologic system where water quality may not be easily predicted by adjacent, upland land use.

A steady-state stream network-mixing model, based on the fundamental principle of conservation of water and dissolved mass, was used to predict the variations in concentrations of dissolved constituents along each mainstem during the synoptic surveys. For each reach  $i$ , the steady-state water balance equation can be written as:

$$Q_{D(i)} = Q_{U(i)} + Q_{T(i)} + Q_{S(i)} + Q_{lat(i)}, \quad (2)$$

where  $Q$  is volumetric discharge and the subscripts D, U, T, S, and lat refer to downstream, upstream, tributary, karst spring, and net lateral inflow, respectively.

Assuming a conservative behavior for a particular dissolved constituent, the corresponding mass balance equation is written as follows:

$$Q_{D(i)}C_{D(i)} = Q_{U(i)}C_{U(i)} + Q_{T(i)}C_{T(i)} + Q_{SS(i)}C_{S(i)} + Q_{lat(i)}C_{lat(i)}, \quad (3)$$

where C is the concentration of the respective dissolved constituent. We explored the utility of two different models: (1) a “base model”; and (2) an “actual flow model”. The “base model” used only the measured concentration data and assumed that the discharge at each station was directly proportional to the corresponding TCA obtained through subwatershed delineation (in effect, the corresponding TCA’s can be substituted for the Q’s in equations (2) and (3)). The “actual flow model” incorporated both the measured concentration and field discharge data. Since  $C_{D(i)}$  and  $Q_{D(i)}$  were measured in the field (or  $Q_{D(i)}$  could be estimated using the respective TCA in the base model), the model was employed to estimate  $C_{lat}$ . Rather than using the model to estimate  $C_{lat(i)}$  for each reach, we used the model to estimate the mean concentration of  $C_{lat}$  across each subwatershed, such that the sum of squares of the differences between predicted and observed concentrations of each constituent in each reach was minimized. The model was implemented in Excel and optimized solutions were obtained using a customized Excel Solver optimized routine that maximized Nash-Sutcliffe efficiency (NSE) (Nash & Sutcliffe, 1970).

### **3.3.7 Data analysis**

Estimated percentages of dominant sources of the mainstem (i.e., lateral groundwater baseflow, karst springs, and tributaries) were calculated using in-field discharge measurements and the steady-state water mass balance equation (Eq. 2). We looked at the source of the mainstem to determine if this affects water quality as opposed

to land use. Further investigation of the spatial variation along the mainstem and the contributing sources of tributaries and karst springs was done using scatter plots with several nutrient and ion constituents. Land use effects (i.e., percent canopy LCA, percent planted riparian forest buffers LCA, and percent forested EHA) on water quality was tested using Spearman's Rank Correlation test (SRC) because of the non-normal distribution of the data — commonly found when collecting water-quality data (Helsel and Hirsch 1992, Miller et al. 1997). Analyses were performed using delta concentrations ( $\Delta C$ ) and net lateral inflow ( $C_{lat}$ ). Simple concentration differences (i.e.,  $\Delta$ 's) were calculated as  $\Delta C = C_D - C_U - C_T - C_S$ . While analyses using concentration differences made use of all of the site data, concentrations of net lateral inflow ( $C_{lat}$ ) could not be calculated for losing reaches; therefore, losing and indefinite reaches were omitted, limiting analysis to 27 sites in spring 2016, 25 sites in fall 2016, and 26 sites in spring 2017 when all mainstem sites were combined (Table 3.2).  $C_{lat}$ 's for gaining reaches were quantified using a steady-state reach mass balance model that neglects in-stream nutrient processing:

$$C_{lat} = \frac{[(Q_{meas,D} * C_D) - (Q_{meas,U} * C_U) - (Q_{meas,T} * C_T) - (Q_{meas,S} * C_S)]}{(Q_{meas,D} - Q_{meas,U} - Q_{meas,T} - Q_{meas,S})} \quad (4)$$

In some instances, estimated  $C_{lat}$ 's were negative where upstream and downstream flow rates were similar and downstream nutrient concentrations were lower than upstream, possibly from in-stream processing and/or experimental error.



Table 3.2 Number of stream segments found in each category (gaining, losing, and indefinite) for each subwatershed (Murleys Branch – MB; Beaver Creek – BC; Little Antietam Creek North – LACN; and Little Antietam Creek South – LACS).

		5% Error Incorporated					
		Gaining	Losing	Gaining	Losing	Indefinite	Total Sites
<b>MB</b>	Spring 2016	12	5	12	2	3	17
	Fall 2016	10	7	10	4	3	17
	Spring 2017	10	7	10	3	4	17
<b>LACN</b>	Spring 2016	6	-	6	-	-	6
	Fall 2016	3	2	3	-	2	5
	Spring 2017	3	2	3	-	2	5
<b>BC</b>	Spring 2016	3	6	3	4	2	9
	Fall 2016	5	2	5	2	-	7
	Spring 2017	7	2	7	2	-	9
<b>LACS</b>	Spring 2016	6	1	6	1	-	7
	Fall 2016	7	-	7	-	-	7
	Spring 2017	6	1	6	-	1	7

*Note: Indefinite refers to streams that were initially found losing but changed to gaining when incorporating 5% measurement error (Sauer and Meyer 1992). Total sites may differ across seasons due to some reaches being dry.*

Stable isotopes of nitrate ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$ ) were used to further understand the processes controlling the nitrate concentration. We used SRC to determine any relationships with LULC. We assumed a positive relationship between canopy, forested EHA, and planted buffers with  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  indicates isotopic fractionation through denitrification. This would be further supported by analyzing the relationships between both  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  with  $\text{NO}_3\text{-N}$ , where a negative relationship would identify denitrification, and  $\delta^{18}\text{O}$  versus  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$ , where a slope between 0.5 and 1 would also provide evidence of denitrification (Kendall et al. 2007). A decline in  $\text{NO}_3\text{-N}$  without the increase in fractionation would support plant uptake, since this method of

nutrient mitigation is found to have small to no isotopic fractionation effect (Mariotti et al. 1982, Kendall 1998, Yoneyama et al. 2001, Dhondt et al. 2003, Granger et al. 2008, Bauersachs et al. 2009, Lutz et al. 2020). Nitrate isotopes were also used as a supplemental line of evidence to determine the extent lateral groundwater and karst springs/ tributaries influence the mainstem.

We used ANCOVA to find any statistically significant differences between percent planted riparian forest buffers on nutrient concentrations while controlling for soil type, geology, and presence/absence of faults and karst. Buffer age was excluded because planting years were all within close range of one another (Table 3.1). Because it may require a few years for riparian forest buffers to become established, we ran another ANCOVA analysis using forested EHA. Significant results (if any) identified factors that could influence future successful planted riparian forest buffers, assuming that percent forested EHA is an accurate representation of a mature buffer (Gold et al. 2001).

### **3.3.8 Combining data with previous study**

Data from the four subwatersheds were combined with previously collected data (from Chapter 2) to estimate the range of potential nutrient reductions across the R&V using a simple linear regression model. Eliminating losing reaches from certain analyses within the individual studies resulted in a small sample size. This small sample size restricts making confident estimations on the amount of nutrients riparian buffers within the R&V could potentially remove from groundwater before it discharges into surface waters. However, because planted forest buffers alone (i.e., special interest sites) in Chapter 2 showed limited utility in reducing nitrogen and phosphorus and the goal was to determine how well riparian forest function within the R&V regardless of deliberate

plantings through CREP or naturally present, all sites were included. We assumed that planted riparian forest buffers will eventually reduce nutrients at the same magnitude as natural forest if managed properly and are preserved long enough to become established and mature.

Using the linear regression model in R we combined all gaining reaches from this study and Chapter 2 and eliminated outliers until all assumptions were met using the global validation of linear model assumptions or 'gvlma' package. The gvlma package tests the relationship for the following: single global test, skewness, kurtosis, nonlinear link function, and heteroscedasticity (Peña and Slate 2006). When any assumption was violated, Cooks distance function in R was used to detect outliers (Robinson et al. 1984). Once outliers were removed from the dataset, the linear regression model was rerun. This process was repeated until all assumptions were met. This was justified to find an accurate constant rate that represents nutrient decline in groundwater per increase in percent forested area. Significant SRC results provided confidence that a relationship exists, but it cannot provide a constant rate. By using the linear regression model and removing the outliers, we assume there are riparian buffers throughout the R&V that are functional and not controlled by unique and complex hydrogeomorphological conditions.

The results of the linear regression model were used to predict nutrient loads for each individual site that was retained in the dataset using a zero and 100% riparian buffer scenario. Estimated nutrient loads from catchments with zero percent buffer were calculated by multiplying the intercept by their measured net lateral groundwater discharge ( $\text{m}^3 \text{s}^{-1}$ ). Loads were converted to  $\text{kg/ha-yr}$  by dividing by the total riparian area. Based on USGS stream gauge data, the median discharge rate was very similar to

the mean long-term runoff rate of Town Creek watershed — the watershed in which many of our study sites are located (U.S. Geological Survey 2021). Using this comparison as validation, we moved forward by using the median found by Microsoft Excel's Descriptive Statistics Tool (2021) of the computed instantaneous nutrient loads to represent annual riparian buffer nutrient reduction. We calculated 95% prediction intervals of the intercept (lower bound and upper bound) to find a range of nutrient reduction loads that would best capture the variation of nutrient reductions when establishing a riparian buffer on a random, individual site within the R&V, assuming the catchment contains hydrological conditions conducive to riparian buffer function. The intercepts were again multiplied by each site's net lateral groundwater discharge and their medians were used to define the minimum and maximum loads.

### ***3.4 Results***

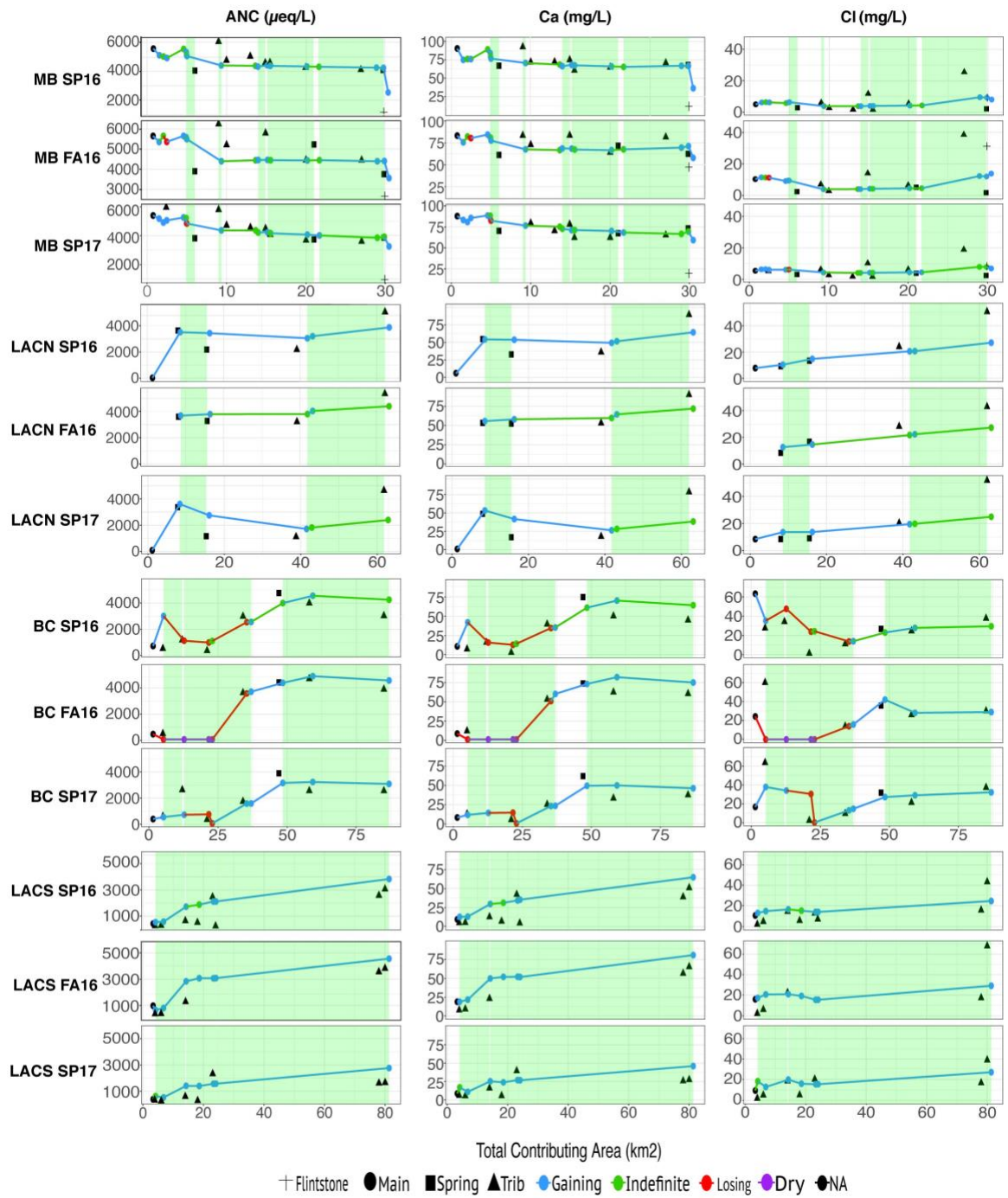
Based on reference maps and observation, karst springs and other unique hydrogeological systems exist throughout the four subwatersheds. In MB, two large karst springs discharge into the mainstem (Murleys Branch Spring and Warm Spring), along with many small springs that were observed during sampling. Flintstone Creek, another major tributary of Town Creek that is separated from MB by a mountain, follows a subsurface flowpath beneath the mountain, surfaces, and joins MB just upstream of the Warm Spring-MB confluence. Geologic maps of the Antietam Creek subwatersheds show the mainstems and tributary channels meandering over faults and multiple types of bedrock, including highly fractured dolomite, sandstone, and shale with sinkholes, depressions, and karst springs located throughout the catchments. BC has one of the largest springs in Maryland (average ~ 11,000 L/min) (Seneca Valley Trout Unlimited,

2018), which serves as the primary source of water for the Albert Powell Fish Hatchery. Two unnamed karst springs were identified in LACN during sampling and while we did not discover any in LACS, the Keedysville & Shepherdstown Quadrangle geologic map shows many karst springs near the LACS tributaries that we sampled (Brezinski 2009, Brezinski and Fauth 2009). Therefore, we assume that some tributaries may be mislabeled or are a mixture of tributary and karst spring — a likely situation in the other subwatersheds.

To understand how stream water chemistry changes along the mainstems with the known contributing sources that we sampled (i.e., lateral inflow, tributaries, and springs), we first plotted constituents thought to be less biologically reactive (i.e., not affected by biological reactions to a first approximation). In all four subwatersheds, Figures 3.3A-B show chemical changes in the mainstems from the headwaters to their final outlets using ANC,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ . Sites are ordered from left to right, representing upstream to downstream with tributaries and springs inserted in their proper location along the mainstem. In MB, all the mainstem and contributing waters had high ANC,  $\text{Ca}^{2+}$ , and  $\text{SO}_4^{2-}$  concentrations. The first karst spring (~6 km<sup>2</sup> TCA) decreased the concentration of ANC and  $\text{Ca}^{2+}$  in the mainstem, where they then remained fairly steady until a decrease in the final downstream site after receiving waters from Flintstone Creek and Warm Spring.  $\text{Cl}^-$  showed the same, but subtler pattern, during the spring seasons when concentrations of Flintstone Creek and the MB mainstem were similar.  $\text{SO}_4^{2-}$  concentrations showed little change until further downstream in response to the last contributing tributary, karst spring, and Flintstone Creek. In LACN, the first karst spring and the last tributary showed the biggest influence in the mainstem's chemical

composition in all three seasons and in all four less biologically reactive constituents. During the fall, the first section of the reach was dry, but the chemistry throughout the mainstem was similar to spring 2016. In the spring 2017 sampling, ANC and  $\text{Ca}^{2+}$  concentrations were lower than the other two seasons; however,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  remained consistent in all three sampling dates. In BC, ANC and ion patterns were similar between the spring sampling dates, but during fall sampling, many of the mainstem sites were dry, validating that much of the mainstem consisted of karst springs and tributary waters. This is supported by the higher ion concentrations at the outlet site compared to the spring seasons. However, in all instances, the mainstem was largely affected by the major karst spring feeding the Albert Powell Hatchery (~50 km TCA). In LACS, all seasons showed their highest concentrations in ions at the outlet, possibly contributed by the last major tributaries. During the fall, one tributary was dry, but it had little impact on the final concentration when comparing to the spring seasons.

a.



b.

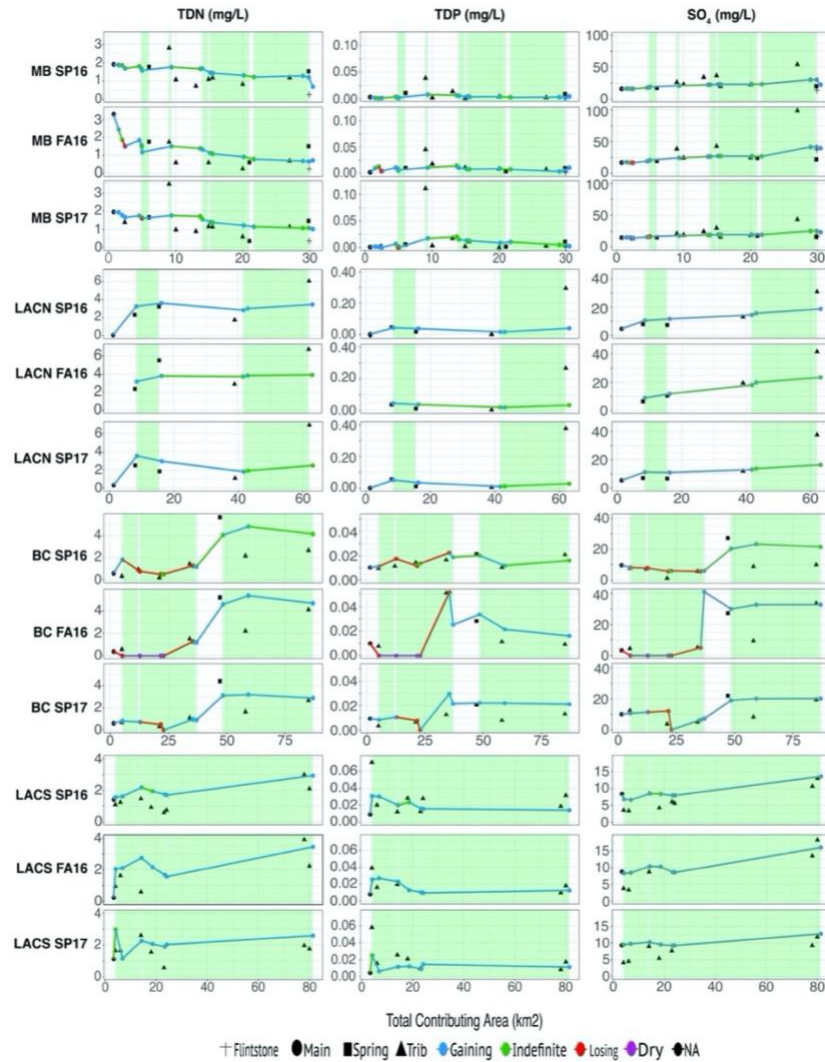


Figure 3.3 (a) Acid neutralizing capacity (ANC) in  $\mu\text{eq/L}$ , and calcium (Ca), chloride (Cl), (b) total dissolved nitrogen (TDN), total dissolved phosphorus (TDP), and sulfate ( $\text{SO}_4$ ) in  $\text{mg/L}$  along the mainstem from upstream to downstream as the total contributing area (TCA) on the x-axis increases. From top to bottom are the following watersheds: Murleys Branch (MB), Little Antietam Creek North (LACN), Beaver Creek (BC), and Little Antietam Creek South (LACS). Each subwatershed has three graphs representing the spring 2016 sampling (SP16), fall 2016 sampling (FA16), and spring 2017 sampling (SP17). Measurements taken along the mainstem are connected by line segments to show more clearly the variation within all of the watersheds. The line colors represent the state of the stream (i.e., “dry”, “gaining”, “losing”, and “indefinite”). Because some of the losing streams were very close to being either positive or negative with a 5% calculated error (Sauer et al. 1992), those were labeled indefinite. Watershed area of springs and tributaries were modified to represent their location/ contribution to the mainstem on the graph. Green transparent background indicates location of buffers along the mainstem.



Nutrient concentrations had a slightly different pattern from the less biologically reactive constituents, but nevertheless showed evidence of tributary and karst spring influence. TDN concentrations decreased slightly where riparian forest buffers were present along the mainstem in MB and in sections of BC in all three sampling seasons; however, majority of the tributaries and karst springs had lower concentrations of TDN than the mainstems. LACN and LACS did not show any reduction in TDN where riparian forest buffers were located, but instead increased in response to contributing tributaries and karst springs with higher concentrations (Fig. 3.3b). Through anecdotal observation,  $\text{SO}_4^{2-}$  concentrations demonstrated a similar pattern to TDN in all three sampling dates in LACN, spring sampling dates only in BC, spring 2016 sampling date in LACS, but none within MB (Fig. 3.3b). TDP concentrations slightly declined where riparian forest buffers were present along the mainstem of MB in all three sampling dates but again, could be in response to the tributaries and karst springs with lower concentrations. BC had the greatest variation in TDP along the mainstem and among the different sampling seasons. One particular BC site showed a dramatic increase in TDP in fall 2016 (TCA ~35 km<sup>2</sup>), where a riparian forest buffer is present, but the reach was deemed 'losing' and the concentration matched the incoming tributary. During the two spring seasons, the reach had a less dramatic increase in TDP concentrations, but the flowrates varied between each season. In all three seasons, LACN and LACS showed no distinct decline of TDP. In all the subwatersheds, the changes in the nutrient concentrations appear to be in response to the mixing of tributaries and karst springs with the mainstems, rather than a nutrient reduction in lateral groundwater from the presence of riparian forest buffers.

A strong correlation between  $\text{NO}_3\text{-N}$  and  $\text{Cl}^-$  indicated nitrate contamination from wastewater across all sites ( $\rho = 0.40$ ;  $p\text{-value} < 0.01$ ) and along the mainstem ( $\rho = 0.53$ ;  $p\text{-value} < 0.01$ ) during the fall, and within karst springs ( $\rho = 1$ ;  $p\text{-value} < 0.01$ ) during the spring 2016 sampling when incorporating all subwatersheds. When analyzing subwatersheds separately, LACS sites showed a significant correlation ( $\rho = 0.87$ ;  $p\text{-value} < 0.01$ ) during spring 2016. Significant positive correlations between  $\text{NO}_3\text{-N}$  and  $\text{SO}_4^{2-}$  that suggests fertilizer as the N source, were not found in the analyses incorporating all sites. When analyzing subwatersheds separately, correlations were found in the BC subwatershed during both spring seasons ( $\rho = 0.77$ ;  $p\text{-value} < 0.01$  and  $\rho = 0.61$ ;  $p\text{-value} < 0.05$ , respectively) and in LACS during spring and fall 2016 ( $\rho = 0.82$ ;  $p\text{-value} < 0.01$  and  $\rho = 0.62$ ;  $p\text{-value} < 0.05$ , respectively).

The statistical model (Eq. 1) using USGS stream gauge and TCA to predict mainstem discharge rates, found the most accurate predictions for MB in spring 2017 (Fig. 3.4A-c,  $\text{NSE} = 0.85$ ); LACN in spring 2016 & 2017 (Fig. 3.4B-a/c,  $\text{NSE} = 0.97$  and  $0.86$ , respectively); BC in spring and fall 2016 (Fig. 3.4C-a/b,  $\text{NSE} = 0.77$  and  $0.67$ , respectively); and LACS in spring 2016 and 2017 (Fig 3.4D-a/c,  $\text{NSE} = 0.87$  and  $0.71$ , respectively). We speculated that a larger than predicted discharge implies a contribution from a karst spring, such as the last point in the MB mainstem in spring 2016 (Fig. 3.4A-a), and a less than expected discharge indicates a losing reach, such as majority of the BC mainstem reaches in spring 2017 (Fig. 3.4C-c). However, only two losing reaches were confirmed using the steady-state water balance equation to find net lateral inflow of groundwater ( $Q_{\text{lat}}$ ) (Table 3.2). The bar graphs below each scatter plot in Figure 3.4 represents the  $Q_{\text{lat}}$ 's normalized by their local contributing area (LCA). We anticipated a

steady inflow of net lateral groundwater where the observed discharge most closely matches the predicted discharge rates. LACN in spring 2016 had the most consistent lateral groundwater (Fig. 3.4B-a) and the highest NSE (0.97) for the USGS model, which supports this hypothesis. LACN in spring 2017 showed very little lateral groundwater inflow and losing reaches along the downstream region of the mainstem. LACS (Fig. 3.4D) showed a seasonal trend in lateral groundwater discharge that was almost identical in the spring seasons. A large amount of net lateral inflow relative to the other sites is also exhibited (site at TCA ~25 km<sup>2</sup>), possibly revealing a hidden karst spring. MB and BC (Fig. 3.4A and 3.4C, respectively) indicated no temporal trends nor consistency in groundwater discharge, thus making it unclear why the USGS model did better in some seasons and not others. Among all of the reaches, normalized lateral discharge rates ranged from  $-7.51 \times 10^{-7}$  m/s to  $5.83 \times 10^{-7}$  m/s (both min and max from MB, spring 2017). Normalized discharge of the tributaries and springs ranged from 0 (indicating intermittent streams in three of the four subwatersheds), to the highest discharge of  $2.51 \times 10^{-6}$  m/s in Flintstone Creek located in MB, spring 2016 (Appendix B) — note: not all true watershed areas are known for karst springs and tributaries. This lack of steady lateral groundwater inflow illustrates the complexity of the hydrological system and heterogeneity across the subwatersheds.

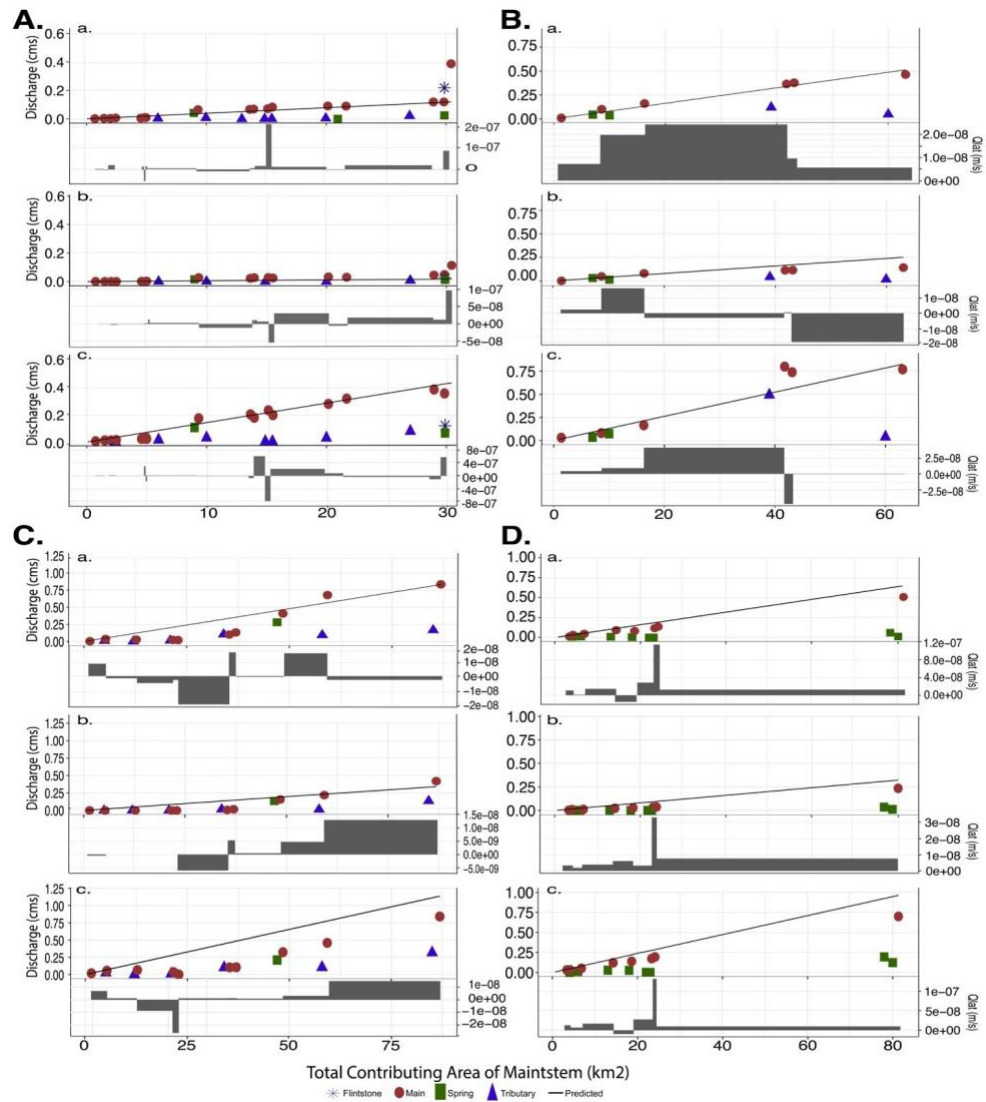


Figure 3.4 Measured discharge of the mainstem, spring, tributaries, and Flintstone Creek (MB only) as a function of total contributing area (TCA) for each watershed. Graphs illustrate how measured and predicted stream discharge varies as a function of TCA across the four subwatersheds. (A) is Murleys Branch, (B) is Little Antietam Creek North, (C) is Beaver Creek, and (D) is Little Antietam Creek South. Figure labels (a.), (b.), and (c.) indicate the different seasons the measurements were taken (a.= spring 2016; b.= fall 2016; c.= spring 2017). Black linear line represents predicted discharge based on watershed area and USGS local stream gauges. TCA of the springs, tributaries, and Flintstone Creek were manipulated to show where they are located along the mainstem; therefore, the x-axis is for the TCA's of the mainstem sites only. Below the scatter plots are barcharts representing the measured lateral groundwater discharge (Q<sub>lat</sub>) normalized to each of the reach's local contributing watershed area. Each bar has been extended to show the locations of each reach (i.e., from its upstream site to its downstream site).

Predominant water sources to the mainstems varied spatially and temporally along with the main sources of each constituent (Fig. 3.5). The mass budget values greater than 100% and less than 0% are due to the sum of inputs from tributaries and karst springs being greater than the total lateral inflow of the mainstem (i.e.,  $Q_{DCD} - Q_u C_u < Q_{TC} + Q_s C_s$ ), possibly from losing reaches, and/or degradation and volatilization of the constituent. The main water sources and constituents displayed different patterns, conveying nutrient loads are not dependent on the dominant water sources. A similar pattern among all constituents and water sources was only shown in LACS during fall 2016 (Fig. 3.5D) and somewhat in spring 2017. In spring 2016,  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$ , and TDP loads were mainly from tributaries, although the dominant water source was lateral groundwater. Tributaries were the main sources of  $\text{PO}_4\text{-P}$  and TDP loads in MB (spring 2017) and LACN (all three seasons) and made up 53% of  $\text{PO}_4\text{-P}$  loads in BC (spring 2017). BC was difficult to interpret given that losing reaches throughout the mainstem heavily affected the results. During the spring seasons, tributaries and karst springs were major water sources to the mainstem, and in the fall it was fairly distributed amongst karst springs, tributaries, and lateral groundwater. However, the large contribution of  $\text{NH}_4\text{-N}$  from karst springs indicates this may not be an accurate representation of the main sources. Depending on where losing reaches occurred throughout the mainstem, a mix of waters (i.e., tributary, spring, and lateral groundwater) would be lost, but a simple mass balance equation only infers loss of lateral groundwater. Nonetheless, from the large bar representing the contribution of  $\text{NH}_4\text{-N}$  loads, we can infer karst springs were a large contributor.  $\text{NO}_3\text{-N}$  and TDN loads came from all sources and showed temporal

variation from the major contributors in each subwatershed, except MB where in all three seasons, karst springs were a major contributor (Fig. 3.5).

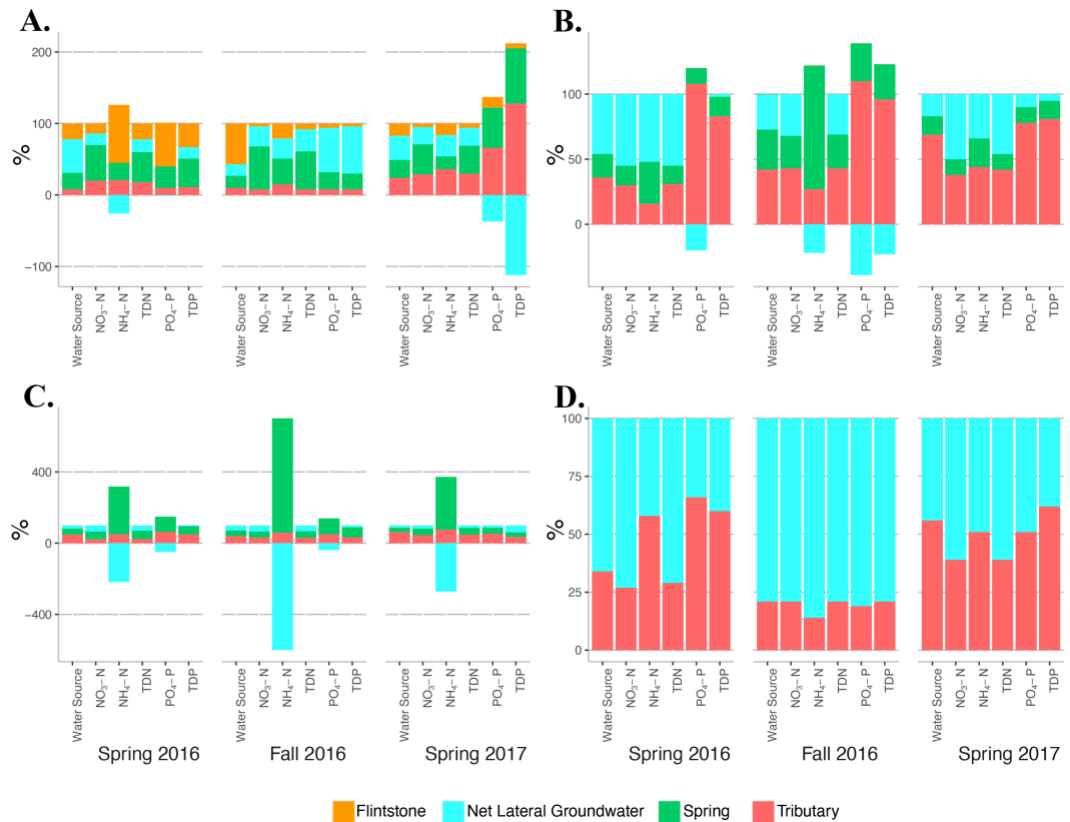


Figure 3.5 Bar charts illustrating the distribution of direct sources of baseflow to the mainstem of (A) Murleys Branch, (B) Little Antietam Creek North, (C) Beaver Creek, and (D) Little Antietam Creek South during three seasons (spring 2016, fall 2016, and spring 2017). Note: since not all springs were likely identified, we have probably underestimated the contributions from springs. Some constituents show the sum of bar length totals greater/less than 100%. This is a result of the non-conservative nature of the nutrients. The total contribution of nutrients from springs and tributaries is higher than the nutrient loads at the final downstream site.

Reaches receiving waters mostly from diffuse lateral groundwater were expected to respond to LULC, while losing reaches were expected to not show much change in water chemistry concentrations. Across all four subwatersheds, the fraction of canopy LCA, planted riparian forest buffers LCA, and forested EHA — hereinafter referred to as canopy, riparian forest buffers, and FEHA, respectively — displayed both negative and

positive relationships on several of the measured stream nutrient concentrations (Table 3.3A/B). However, we found most of the statistically significant correlations ( $p$ -value  $\leq 0.05$ ) occurred during the fall season compared to the two spring sampling seasons (2016 & 2017). During the fall, 44 percent of relationships were in response to riparian forest buffers, but some were positive (i.e.,  $\Delta\text{NO}_3\text{-N}$  ( $\rho=0.37$ ) and  $\Delta\text{TDN}$  ( $\rho=0.34$ )) (Table 3.3A). During the spring and fall 2016 sampling, other positive relationships were found between delta concentrations ( $\Delta\text{PO}_4\text{-P}$  and  $\Delta\text{TDP}$ ) and canopy. As stated earlier, analyses using delta concentrations incorporated gaining, losing, and indefinite reaches, where we expected no response to LULC.

When analyzing nutrient concentrations of net lateral groundwater ( $C_{\text{lat}}$ ) that incorporated gaining reaches only (Fig. 3.3B), all statistically significant relationships exhibited negative correlations, including between riparian forest buffers and  $\text{NO}_3\text{-N}$  and TDN (both  $\rho= -0.51$ ) during the fall season (the same constituents indicating a positive correlation using  $\Delta$ ). Similarly, strong negative correlations were also found between canopy and  $C_{\text{lat}}$  of  $\text{NO}_3\text{-N}$  ( $\rho= -0.70$ ) and TDN ( $\rho= -0.72$ ) in the fall. Within the two spring sampling seasons, only one relationship was found with riparian forest buffers (i.e.,  $C_{\text{lat}}$   $\text{NO}_3\text{-N}$  in spring 2016 ( $\rho= -0.39$ )). Several significant negative relationships were found between FEHA and nutrients in all three seasons, but the species of N and P varied. In spring and fall 2016, TDN declined ( $\rho= -0.41$  and  $-0.48$ , respectively) and in spring 2017,  $\text{NH}_4\text{-N}$  ( $\rho= -0.46$ ),  $\text{PO}_4\text{-P}$  ( $\rho= -0.47$ ), and TDP ( $\rho= -0.40$ ) declined in response to increased FEHA. Overall, nutrients showed the most consistent response to canopy among all three seasons, indicating that stream water quality depends more on upland land use.

Significant relationships between nutrients and LULC were validated by testing correlations for constituents that are less biologically reactive (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , ANC); we did not expect these constituent concentrations to show any significant relationships to canopy or forest cover. No significant relationships were found when incorporating all sites ( $\Delta$ , Table 3.3A), but a few significant relationships were found with gaining reaches ( $\text{C}_{\text{lat}}$ , Table 3.3B). Significant negative relationships were found between  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and canopy, and between  $\text{Br}^-$ ,  $\text{Mg}^{2+}$  and FEHA. Further investigation discovered that the significant relationship between  $\text{Mg}^{2+}$  and canopy in spring 2017 was driven by two outliers, which became nonsignificant once sites were removed. All other constituents showed evidence of a significant response to landcover, although there may be some explanation to these relationships.

Recent research has found that  $\text{Cl}^-$  is not completely conservative in forest ecosystems and undergo a complex biogeochemical cycle (Öberg and Sandén 2005, Bastviken et al. 2007, 2009, Svensson et al. 2012).  $\text{Cl}^-$  can become immobilized through vegetation and microbial uptake, as well as through ion exchange, iron and aluminum oxide adsorption, or converted into organic forms (Svensson et al. 2012). Sequestering through vegetation uptake may explain the negative relationship with canopy. Additionally, harvesting and disturbance of vegetation has been found to release  $\text{Cl}^-$  (Lovett et al. 2005, Svensson et al. 2012), which the alternative upland land use to canopy is agriculture. Therefore, the relationship may also be explaining a positive relationship between  $\text{Cl}^-$  and cropland. In rural areas, synthetic fertilizer (potash ( $\text{KCl}$ )), animal feed, manure, and feedlots can be a major  $\text{Cl}^-$  source to surface and groundwater



(Mullaney et al. 2009, Overbo et al. 2021). The use of potash may also explain the significant decline of  $K^+$  from canopy increase.

$Br^-$  is found naturally in the earth's crust, seawater, and shale geologic formations (Good and Vanbriesen 2019), and anthropogenic sources such as pesticides, herbicides, biocides, disinfectants, coal-fired power plants, and water treatment (Vainikka and Hupa 2012, Mctigue et al. 2014, Winid 2015, Good and Vanbriesen 2019). The  $Br^-$  concentrations in our study sites were low (2.9 – 30.5  $\mu\text{g/L}$ ) and were within range of natural bromide concentrations found in inland groundwaters (3.2 – 58  $\mu\text{g/L}$ ) and lower than concentrations typically found in inland fresh surface waters (14 – 200  $\mu\text{g/L}$ ). The  $Br^-$  in these study reaches are most-likely from natural sources and decline from the increase in canopy and FEHA due to plant uptake (Kung 1990, Yuita 1994, Neal et al. 1997, Hughes et al. 1998).  $Mg^{2+}$  is derived from atmospheric deposition, dissolution of carbonate and silicate rocks, and from anthropogenic sources such as fertilizer.  $Mg^{2+}$  is very mobile, but an essential element for plant growth (Gransee and Führs 2013, Nitzsche et al. 2019); therefore, the negative relationship between canopy and FEHA is most-likely due to vegetation uptake and/ or reduction of agricultural landuse where fertilizer may be applied.

Table 3.3 Statistically significant ( $P < 0.5$ ) relationships between (A)  $\Delta C$  (all reaches) and (B)  $C_{lat}$  (gaining reaches only) (dependent variables) versus % canopy, % forested EHA, & % planted RFB LCA (independent variables) from Spearman's Rank Correlation (SRC) for four subwatersheds (together ('All') and separately) for three sampling seasons (2 spring and 1 fall).

A		% Canopy		% FEHA		% Planted Buffer	
$\Delta$	Season	P-Value	$\rho$	P-Value	$\rho$	P-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	0.10	0.27	0.31	0.17	0.86	0.03
	Fall '16	0.49	0.12	0.78	0.05	0.13	0.26
	Spring '17	0.34	0.16	0.71	0.06	0.34	0.16
<b>NH<sub>4</sub>-N</b>	Spring '16	0.18	0.22	0.69	0.07	0.72	0.06
	Fall '16	0.43	0.14	0.95	0.01	0.28	0.19
	Spring '17	0.47	0.12	0.61	-0.09	0.65	0.08
<b>TDN</b>	Spring '16	0.10	0.27	0.31	0.17	0.41	0.14
	Fall '16	0.57	0.10	0.95	0.01	0.42	0.15
	Spring '17	0.31	0.17	0.75	0.05	0.37	0.15
<b>PO<sub>4</sub>-P</b>	Spring '16	<b>0.04</b>	<b>0.34</b>	0.35	0.16	0.80	-0.04
	Fall '16	<b>0.02</b>	<b>0.40</b>	0.23	0.21	0.47	0.13
	Spring '17	0.11	0.27	0.87	0.03	0.33	0.17
<b>TDP</b>	Spring '16	<b>0.01</b>	<b>0.40</b>	0.28	0.18	0.95	-0.01
	Fall '16	0.07	0.31	0.29	0.18	0.33	0.17
	Spring '17	0.09	0.29	0.84	0.03	0.91	0.02
<b>TOC</b>	Spring '16	0.69	0.07	0.97	0.01	0.70	0.06
	Fall '16	0.63	0.09	0.75	0.06	0.12	0.27
	Spring '17	0.82	0.04	0.81	0.04	0.26	0.19
<b>Ca</b>	Spring '16	0.54	0.10	0.32	0.16	0.91	0.02
	Fall '16	0.86	-0.03	0.54	0.11	0.69	0.07
	Spring '17	0.37	-0.15	0.78	-0.05	0.68	0.07
<b>Cl</b>	Spring '16	0.06	0.31	0.07	0.30	0.89	-0.02
	Fall '16	0.75	0.06	0.58	0.10	0.34	0.17
	Spring '17	0.36	0.15	0.60	0.09	0.50	0.11
<b>Br</b>	Spring '16	0.18	0.22	0.48	0.12	0.96	0.01
	Fall '16	0.49	0.12	0.36	0.16	0.27	0.19
	Spring '17	0.65	0.08	0.59	0.09	0.41	0.14
<b>K</b>	Spring '16	0.24	0.19	0.37	0.15	0.86	0.03
	Fall '16	0.86	0.03	0.92	-0.02	0.13	0.26
	Spring '17	0.81	0.04	0.92	-0.017	0.34	0.16
<b>Mg</b>	Spring '16	0.34	0.16	0.30	0.17	0.72	0.06
	Fall '16	0.98	0.00	0.74	0.06	0.28	0.19
	Spring '17	0.74	-0.07	0.98	-0.004	0.65	0.08
<b>ANC</b>	Spring '16	0.47	0.12	0.31	0.17	0.41	0.14
	Fall '16	0.92	-0.02	0.57	0.10	0.42	0.15
	Spring '17	0.44	-0.13	0.94	-0.01	0.37	0.15

<b>B</b>		<b>% Canopy</b>		<b>% FEHA</b>		<b>% Planted Buffer</b>	
<b>C<sub>lat</sub></b>	<b>Season</b>	<b>P-Value</b>	<b>ρ</b>	<b>P-Value</b>	<b>ρ</b>	<b>P-Value</b>	<b>ρ</b>
<b>NO<sub>3</sub>-N</b>	Spring '16	<b>1.7E<sup>-03</sup></b>	<b>-0.59</b>	0.07	-0.36	<b>0.05</b>	<b>-0.39</b>
	Fall '16	<b>1.7E<sup>-04</sup></b>	<b>-0.70</b>	0.07	-0.37	<b>0.01</b>	<b>-0.51</b>
	Spring '17	<b>0.05</b>	<b>-0.40</b>	0.09	-0.34	0.94	0.02
<b>NH<sub>4</sub>-N</b>	Spring '16	0.53	-0.13	0.53	-0.13	0.42	0.16
	Fall '16	0.89	0.03	0.20	-0.26	0.88	-0.03
	Spring '17	0.46	-0.15	<b>0.01</b>	<b>-0.48</b>	0.58	0.11
<b>TDN</b>	Spring '16	<b>2.2E<sup>-03</sup></b>	<b>-0.58</b>	<b>0.04</b>	<b>-0.41</b>	0.18	-0.27
	Fall '16	<b>8.3E<sup>-05</sup></b>	<b>-0.72</b>	<b>0.02</b>	<b>-0.48</b>	<b>0.01</b>	<b>-0.51</b>
	Spring '17	<b>0.04</b>	<b>-0.40</b>	0.06	-0.38	0.88	0.03
<b>PO<sub>4</sub>-P</b>	Spring '16	0.63	-0.10	0.31	0.20	0.82	-0.05
	Fall '16	0.90	0.03	0.20	0.26	0.80	-0.05
	Spring '17	<b>0.05</b>	<b>-0.38</b>	<b>0.02</b>	<b>-0.44</b>	0.88	-0.03
<b>TDP</b>	Spring '16	0.69	-0.08	0.69	0.08	0.80	-0.05
	Fall '16	0.47	-0.15	0.23	0.25	0.27	-0.23
	Spring '17	<b>0.01</b>	<b>-0.49</b>	<b>0.02</b>	<b>-0.45</b>	0.52	0.13
<b>TOC</b>	Spring '16	0.15	-0.29	0.19	-0.26	0.17	0.28
	Fall '16	0.33	-0.20	<b>0.05</b>	<b>-0.40</b>	0.70	0.08
	Spring '17	0.21	-0.25	0.23	-0.25	0.78	0.06
<b>Ca</b>	Spring '16	0.09	-0.34	0.16	-0.28	0.15	-0.29
	Fall '16	0.22	-0.25	0.35	-0.19	0.39	-0.18
	Spring '17	0.63	-0.10	0.89	-0.03	0.15	-0.29
<b>Cl</b>	Spring '16	<b>4.4E<sup>-03</sup></b>	<b>-0.55</b>	0.12	-0.32	0.47	-0.15
	Fall '16	<b>4.7E<sup>-03</sup></b>	<b>-0.55</b>	0.09	-0.34	0.47	-0.15
	Spring '17	<b>4.8E<sup>-03</sup></b>	<b>-0.54</b>	0.04	-0.40	0.33	-0.20
<b>Br</b>	Spring '16	<b>3.6E<sup>-03</sup></b>	<b>-0.56</b>	<b>0.02</b>	<b>-0.47</b>	0.99	3.4E-03
	Fall '16	<b>0.04</b>	<b>-0.42</b>	0.51	-0.14	0.98	-6.2E-03
	Spring '17	0.31	-0.21	0.42	-0.17	0.96	-0.01
<b>K</b>	Spring '16	0.57	-0.12	0.80	-0.05	0.61	0.10
	Fall '16	<b>0.02</b>	<b>-0.46</b>	0.08	-0.35	0.80	-0.05
	Spring '17	0.12	-0.31	0.10	-0.33	0.61	-0.10
<b>Mg</b>	Spring '16	0.07	-0.36	0.11	-0.32	0.42	-0.16
	Fall '16	<b>0.01</b>	<b>-0.51</b>	<b>0.01</b>	<b>-0.54</b>	0.06	-0.37
	Spring '17	<b>0.04</b>	<b>-0.42</b>	0.11	-0.32	0.14	-0.30
<b>ANC</b>	Spring '16	0.17	-0.28	0.20	-0.26	0.09	-0.34
	Fall '16	0.64	-0.10	0.59	-0.11	0.95	-0.01
	Spring '17	0.54	-0.12	0.73	-0.07	0.11	-0.32

Note: Dependent variables were expressed in mg/l during analysis.

\*EHA = Eco-hydrologically Active, referring to riparian area

\*LCA = local contributing area

\*RFB = Riparian forest buffers

Few statistically significant relationships were found when analyzing individual subwatersheds (Appendices C-J). MB showed the most responses to FEHA in all three sampling seasons. Results uncovered positive relationships with  $\Delta\text{PO}_4\text{-P}$  ( $\rho=0.50$ ) during spring 2016 and  $C_{\text{lat}}$  TDP during the fall ( $\rho=0.62$ ), but negative correlations were found with  $C_{\text{lat}}$  DOC in the fall ( $\rho=-0.66$ ) and  $C_{\text{lat}}$   $\text{NH}_4\text{-N}$  in spring 2017 ( $\rho=-0.64$ ) (Appendices C-D). In LACS, another positive correlation was discovered between  $\Delta\text{NH}_4\text{-N}$  and riparian forest buffers ( $\rho=0.79$ ), but no other significant relationships were found within this subwatershed (Appendices I-J). In BC,  $C_{\text{lat}}$  of  $\text{NH}_4\text{-N}$  and DOC declined with an increase in riparian forest buffers (both  $\rho=-0.95$ ) in the fall season (Appendix H). However, the maximum percent of planted buffer was just over 2% in the LCA, and one site was significantly low compared to the other sites in both of these constituents, driving the slope. We, therefore, surmise these results as a statistical type I error demonstrating a false significant decline in  $\text{NH}_4\text{-N}$  and DOC in response to planted buffers. No significant relationships were found in LACN, but this subwatershed had the fewest sites (Appendices E-F).

Within the individual subwatersheds, several relationships were again found between the less biologically reactive constituents and landcover. LACS showed a significant positive relationship with  $\Delta\text{Mg}^{2+}$  and canopy during the fall, which is when most leaching of  $\text{Mg}^{2+}$  occurs because of less nutrient uptake from vegetation (Appendix I). The amount of  $\text{Mg}^{2+}$  lost depends on the soil pH and cation exchange capacity (Gransee and Fühns 2013). Additional significant relationships found incorporating gaining reaches only ( $C_{\text{lat}}$ ) includes MB with negative correlations between  $\text{Cl}^-$  and planted buffer and  $\text{Mg}^{2+}$  and canopy (Appendix D); BC with a negative and a positive

correlation between Mg and canopy and planted buffer, respectively, but during different seasons (Appendix H); and LACS with negative correlations between Ca/ANC and FEHA (Appendix J). Some of these results were driven by outliers and once removed, were no longer significant (i.e., MB: Cl and planted buffer; BC: Mg and canopy/planted buffer). Scatterplots of the significant relationships found in LACS indicated actual declines of Ca and ANC with increase of FEHA. ANC typically increases in subsurface flows with longer residence time that allows for more interaction with minerals, such as calcium carbonate that is dominant in karst. The significant negative response of Ca and ANC to FEHA, it is different than what we would expect. A more forested watershed would produce higher infiltration rates and slower subsurface flow that would allow for more water-rock geochemical reactions (Rice et al. 2004, Ito et al. 2005).

When merging sites from Chapter 2 to estimate potential nutrient reduction loads in the R&V using a simple linear regression model, a statistically significant relationship between TDN with percent forested riparian area was found incorporating all gaining reaches ( $p\text{-value}=1.4E^{-05}$ ,  $n=102$ ) but did not meet any assumptions. All assumptions were met after rerunning the linear model five times and removing 26 outliers ( $F(1,74)=18.03$ ,  $p\text{-value}=6.2E^{-05}$ ;  $R^2=0.2$ ;  $n=76$ ). The intercept used to calculate load retention was 2.0 mg/L with a slope of -0.02 (Fig. 3.6). A significant correlation was found between TDN and percent forested riparian area each time the linear model was run ( $p\text{-value}<0.05$ ). No significant results were found for the phosphorus species (i.e.,  $PO_4\text{-P}$  and TDP) (Fig. 3.7).

The results using Microsoft Excel's Descriptive Statistics Tool (2021) of the TDN load retention showed that the arithmetic mean of the distribution was much higher than the median value for both TDN loads ( $\bar{x}$  = 195 & median = 64 kg/ha-yr) and measured net discharge rates ( $\bar{x}$  = 1670 & median = 429 mm/yr), indicating that both distributions were right-skewed. Based on USGS stream gauge data, the median discharge rate is actually very similar to the mean long-term runoff rate of Town Creek Watershed (384 mm/yr), the watershed in which many of our study sites are located (U.S. Geological Survey 2021). Using this comparison as validation, we moved forward by using the median of the computed instantaneous TDN loads to represent annual riparian buffer nutrient reduction. The calculated 95% prediction intervals of the intercept (lower bound: 0.2 and upper bound: 4.0 mg/L) was used to find a range of TDN reduction loads that would best capture the variation of nutrient reductions when establishing a riparian buffer on a random, individual site within the R&V. The intercepts were again multiplied by each site's net lateral groundwater discharge and their medians were used to define the minimum and maximum loads, which were 6.4 and 64.2 kg/ha-yr, respectively. General descriptive statistics were the same for the original linear regression model and the upper bound intercept because they both had a positive, non-zero TDN load in the 100% forested riparian area scenario. Therefore, when calculating the difference between the loads using the two scenarios (i.e., 100% and 0% buffered area) the differences remained the same even though the upper bound intercept predicted higher loads in both scenarios.

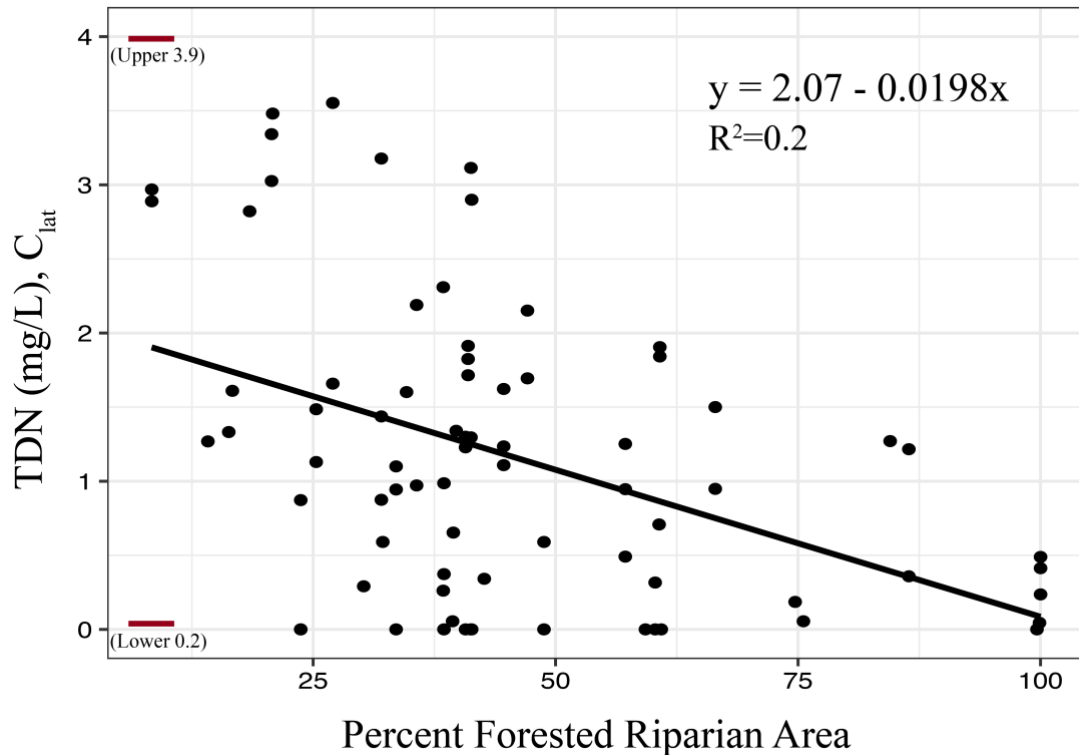


Figure 3.6 Relationship between TDN concentration in net lateral groundwater versus % forested riparian area. The results of the 95% prediction intervals of the intercept are shown by the red horizontal lines.

Nitrate isotopic data did not show strong evidence of denitrification across the subwatersheds, as relationships incorporating all sites showed negative correlations between LULC and  $\text{NO}_3\text{-N}$  isotopes (instead of positive relationships). Other signals of denitrification are a negative relationship between  $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  and  $\text{NO}_3\text{-N}$  and a slope of 0.5 to 1 between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$ . Data uncovered positive relationships between  $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  and  $\text{NO}_3\text{-N}$  (details in Appendix K), but  $\delta^{18}\text{O}$  versus  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  for all sites resulted in a significant slope of 0.4 ( $R^2=0.31$ ;  $p\text{-value} < 0.01$ ) but violated linear model assumptions (i.e., skewness and heteroscedasticity). Analyzing the mainstem sites and tributaries separately produced a significant slope of 0.5 ( $R^2=0.21$ ;  $p\text{-value} < 0.01$ ) and 0.4 ( $R^2=0.33$ ;  $p\text{-value} < 0.01$ ) that met all assumptions. A caveat to analyzing all sites

together is that they are from different sampling seasons — Antietam Creek samples (i.e., LACN, BC, and LACS) were from spring 2016 and MB samples were from spring 2017 — thus, making it inappropriate to compare the isotope analyses with results in Table 3.3. Independent of sampling date, we further assessed the possibility of finding isotopic fractionation in reaches with riparian forest buffers by running a Welch Two Sample t-test against the  $C_{lat}$  and  $\Delta$  of  $\delta^{15}N$  and  $\delta^{18}O_{NO_3-N}$  for sites with and without buffers. No significant differences were found across the two categories, but this does not exclude the possibility of nutrient reduction through plant uptake.

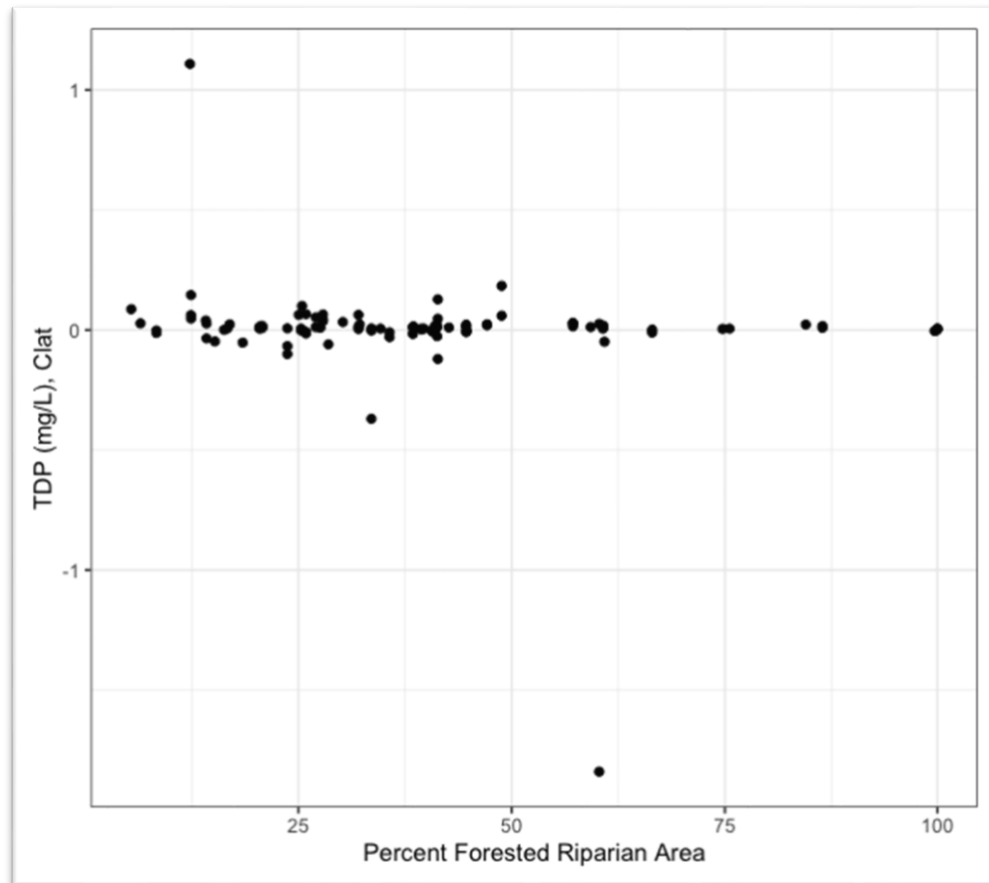


Figure 3.7 Relationship between TDP concentration (mg/L) in net lateral groundwater versus % forested riparian area. Relationship was not significant (p-value=0.14).



When analyzing subwatersheds separately, LACN, LACS, and MB exhibited results supporting denitrification. Relationship between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  from all sites within LACN subwatershed produced a significant slope (p-value < 0.01) of 0.68 that met all assumptions. LACS showed evidence of fractionation of  $\Delta\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  in response to FEHA (SRC,  $\rho=0.89$ ,  $P = 0.012$ ). Nonetheless, a significant negative relationship was not found between FEHA and  $\Delta\text{NO}_3\text{-N}$  (Table 3.3). In MB, a negative relationship was found between raw concentrations of  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  and  $\text{NO}_3\text{-N}$  ( $\rho=-0.51$ ,  $P = 0.004$ ). Table 3.3 showed no significant correlations between  $\text{NO}_3\text{-N}$  and LULC in MB spring 2017, but TDN and  $\text{NH}_4\text{-N}$  did show a response to canopy and FEHA, respectively. Relationship between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  incorporating all MB sites also produced a significant slope (p-value < 0.01) of 0.60. Other significant relationships were found between nitrate and LULC with nitrate isotopes that were not indicative of denitrification but are described in Appendix L.

Scatterplots of  $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  provided some evidence about the sources and biological processes of N in each of the study reaches (Appendices M–P). In LACN, plots of  $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  and  $\text{NO}_3\text{-N}$  indicated both mixing and denitrification with nitrate declining and fractionation increasing along the mainstem (Appendix N). A high concentration of  $\text{NO}_3\text{-N}$  in the outlet site was most likely from the final tributary that was high in  $\text{NO}_3\text{-N}$  and  $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  (indicating a source from pasture or septic system, which can be validated from the LULC shown in Fig. 3.2B for this site). Fractionation of  $\text{NO}_3\text{-N}$  isotopes indicated denitrification along the mainstems of MB (Appendix M) and BC (Appendix O). In MB,  $\text{NO}_3\text{-N}$  declined with increased fractionation until waters merged with a major tributary and spring (Flintstone Creek and Warm Springs,

respectively). BC's mainstem showed similar results until merging with the Powell Hatchery karst spring. High  $\text{NO}_3\text{-N}$  and the isotopic composition of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  indicates that the spring was high in  $\text{NH}_4^+$  fertilizer (Kendall et al. 2007, Lutz et al. 2020). LACS (Appendix P) showed mixing with tributaries containing low  $\text{NO}_3\text{-N}$  and high  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  indicating deep upwelling water due to the exposure to more fractionation processes like denitrification (Mariotti et al. 1988). The final site was relatively high in  $\text{NO}_3\text{-N}$  and  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$ , possibly from manure that is generally enriched in  $\delta^{15}\text{N}$  (Lutz et al. 2020). In this subwatershed, high proportions of cropland and pasture encompass the LCAs of the final tributary and mainstem site (Fig. 3.2D).

After assessing the potential hydrological controls on riparian forest buffers and gathering evidence of biological processes and nitrogen sources using nitrate isotopes, our next goal was to identify any factors impeding the function of riparian forest buffers. We conducted a one-way ANCOVA to compare the effectiveness of percent riparian forest buffers on nutrients while controlling for soil type, geology (bedrock present at site), presence/absence of faults, presence/absence of karst, and buffer age. Although our data are not normally distributed, ANCOVA was used for its robustness. No significant responses were found, indicating that none of the covariates we selected had much influence over the function of riparian forest buffers in the R&V as a whole. A few significant results were found when partitioning the subwatersheds, but this decreased the sample size and removed the number of possible covariates that would justify these results. Because these sites were chosen based on other parameters, we suggest choosing sites based specifically on these different levels of covariates if they are to be properly tested.

Finally, we applied the steady-state stream network mixing model to characterize spatial variations in stream water nutrient concentrations and loads using each of the measured constituents within and among the four basins in the R&V province. Two versions of the model were employed: a “base model” and an “actual flow model” (described in Methods section) with optimal solutions based on minimizing errors using a Nash-Sutcliffe model efficiency (NSE) coefficient. Model performances were evaluated based on the NSE, as well as the root mean square error (RMSE) (Appendices Q–T). Results showed that the “actual flow model” is superior to the “base model” for predicting mainstem concentrations. This is supported by all three sampling dates for BC and MB, finding the “actual flow model” to be a better predictor for majority of the constituents. Models were equivalent for LACN, but the “actual flow model” was best at predicting majority of the constituents for spring 2016 sampling dates, “base model” was better at predicting constituents for the spring 2017 sampling dates, and models were equal for fall 2016. For LACS, “base model” was superior for all three sampling dates. Pearson’s Chi-square test found a difference in superiority of the models based on the subwatersheds, ( $\chi^2(3, N=4) = 48.3, P = 1.8E-10$ ) but found no significance between seasons nor the constituents being predicted. Details of which model was best at predicting constituents for each individual subwatershed are given in Appendix U.

### ***3.5 Discussion***

We designed our study to examine how the direction and magnitude of lateral groundwater and the predominant sources of a mainstem affect water quality and its response to riparian forest buffers across karst landscapes. We hypothesized the mainstem would be a mix of gaining and losing reaches, with at least half of the gaining

reaches dominated by tributaries and karst springs that would affect nutrient concentrations, rather than LULC. Overall, we found water quality depends on the predominant water sources of the mainstem (i.e., lateral groundwater, tributaries, and karst springs) and the land use of the watershed, and potentially of those adjacent, which supports some of our hypotheses. We also found the predominant water sources of the mainstem varied spatially and temporally, along with the major sources for each measured constituent. The number of gaining and losing reaches found within each mainstem also showed temporal variability. Given the high heterogeneity of streamwater sources and direction and magnitude of groundwater, we did not find clear evidence that riparian forest buffers are effective in reducing nutrients throughout the R&V.

Despite not finding clear evidence, a few results showed nutrient reductions with riparian forest buffer presence. The current paradigm of nutrient filtering by riparian forest buffers suggests they will be most effective in locations where lateral groundwater is the predominant water source and a hydrologic connection exists between the nutrient source, the buffered area, and the stream (Lowrance et al. 1997). Subwatersheds that exhibited groundwater as the predominant water source were LACS in spring and fall 2016, and those that almost had an equal distribution of lateral groundwater and other sources were MB and LACN in spring 2016 and LACS in spring 2017. Of this selection, no significant negative correlations were found between LULC and nutrients. MB sites demonstrated the most correlations between nutrients and land use compared to the other subwatersheds but were in fall 2016 and spring 2017 (Appendix D) when only 16% and 34% of the mainstem was lateral groundwater, respectively. In another study that focused on how land cover and geology affect water quality, cropland had a marginally positive

relationship with nitrate in the Great Valley of the R&V (similar location to the Antietam sites) and no relationship with forested catchments. In what they considered the Appalachian Mountains of the R&V (similar location to the MB sites), positive and negative relationships with nitrate were found with cropland and forest, respectively. They attributed the lack of relationships between nutrients and land use in the Great Valley to its geology (i.e., carbonate rock) (Liu et al. 2000). However, the relationships in MB are not very clear. In fall 2016, net lateral groundwater had the highest contribution to  $C_{lat}$  TDP which had a significant correlation with FEHA, but the relationship was positive. The other significant relationship was between  $C_{lat}$  TDN and canopy in spring 2017, but a mix of water sources contributed to its concentration.

When incorporating all sites together, several correlations were observed between nutrients and land use.  $C_{lat}$   $\text{NO}_3\text{-N}$  and TDN both declined in response to riparian forest buffers in the fall, but a stronger, negative correlation with percent canopy was also found, indicating nutrient concentrations are dependent on upland land use rather than the presence of riparian forest buffers (Table 3.3B). Geology in this region has also been shown to preserve high concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  from agricultural activity in the groundwater from the carbonate lithology that rapidly transports soluble N to nearby streams. Sites within the R&V exhibiting lower concentrations of N had predominantly forested catchments (Miller et al. 1997) and the main source was attributed to atmospheric deposition (Jaworski et al. 1992, Miller et al. 1997). In general, less significant relationships were found between land use and variations of phosphorus. This can be attributed to measuring only soluble forms of P. Most forms of phosphorus bind to

soil particles and are only released during storm events (Jordan et al. 1997b, Liu et al. 2000), which we did not sample.

Another hypothesis for our lack of significant findings between nutrients and riparian forest buffers is any potential nutrient retention within groundwater is most likely masked from large contributions of tributaries/karst springs. Our efforts to detect nutrient concentrations from net lateral inflow ( $C_{lat}$ ) by subtracting nutrients from the upstream site and other contributing sources, assumes we identified all of them. However, karst springs carrying baseflow are often hidden that can affect water budgets (Worthington 1991). The net lateral discharges shown in Figure 3.4 illustrates variability and complexity throughout the mainstems, making it difficult to confirm all incoming waters were captured. For instance, we believe a tributary may have been missed in LACS just before the final mainstem site. The high-resolution stream map we used to define our study sites indicated a large tributary but during sampling we failed to locate it and presumed it to be dry. Compared to our map, USGS Streamstats also shows a tributary based on their algorithm, although much smaller. Streamstats database calculated a 14.5 km<sup>2</sup> drainage basin with 97% underlain by limestone (USGS, 2016). ANC, Ca<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup> have been linked to water sources reacting with carbonate bedrock and oxidation of pyrite in limestone (Miller et al. 1997, Liu et al. 2000). A missed tributary would explain the high concentrations of these constituents in the last downstream site of the mainstem that surpasses concentrations of the last two tributaries.

ANC and ion data effectively show how tributaries and karst springs influence the chemistry of the mainstems. Whether riparian forest buffers successfully reduce nutrients in lateral groundwater, the dominant sources of the mainstem (i.e., diffuse lateral

groundwater, karst springs, and tributaries) also control nutrient loads. Obvious changes along the mainstem from these inputs are shown in Figure 3.3a, which are similar to results reported by Gburek & Folmar (1999) for a tributary of the Susquehanna River within the R&V and Bohlke et al. (1995) for a watershed near Locust Grove, Maryland. Gburek and Folmar (1999) found ion (e.g., Ca, Mg, SO<sub>4</sub>, Cl, NO<sub>3</sub>, and HCO<sub>3</sub>) concentrations in streams depended on discharges from tributaries, where intensity depended on the land use from where they originated — higher concentrations were from heavily manured sites and low ion concentrations were from primarily forest (Gburek and Folmar 1999b). Figure 3.2 shows land use of each reach, including the last tributary of LACN (Fig. 3.2B) that slightly increases TDN and TDP in the last downstream site of the mainstem. High concentrations of constituents can be explained by the large proportion of cropland and pasture within the tributary's LCA. In Bohlke et al. (1995), they found discharge from deeper aquifers containing old groundwater as the primary controller of the stream water quality (Bohlke and Denver 1995). Some tributaries and karst springs in our watersheds are presumed to contain older waters where water quality cannot be easily explained by land use and according to figure 3.7, can be the main source of nutrients.

How tributaries and karst springs influence the chemistry of the mainstems varies temporally. All subwatersheds had a greater contribution from tributaries to the mainstem in spring 2017 than in spring 2016, while net lateral groundwater contributed less on a percentage basis. One explanation is more frequent rain events occurred during the late winter and early spring season in 2017 than in 2016 before sampling. Although stormflow conditions were avoided by referencing the USGS hydrographs, most sources' average discharge rates (i.e., lateral groundwater, karst springs, and tributaries) were

higher during spring 2017 than spring 2016 (Fig. 3.4). The higher discharge rates may be a response to the larger volume of recharge received from the rain events that accumulated over several months. Characteristics of the tributaries are unknown and may be misidentified karst springs. In karst systems, the quick response time after a rain event, termed “quickflow,” is thought to be drainage of conduits, while a slower response, termed “slowflow”, is drainage of the fractures into the conduits. One study analyzing hydrographs from karst springs concluded 50% of spring discharge was by quickflow and 50% by slowflow (Atkinson 1997). The amount of water contributed from each source and its discharge rate depends on its aquifer’s storage capacity and its drainage system, where there is tremendous variation across karst landscapes (White 2002).

We also considered the LULC defined for these subwatersheds may be inaccurate because catchment delineation tools in ArcGIS do not consider subsurface hydrological processes, thus potentially marking a false boundary in karst landscapes (Jie Luo et al. 2016). While some tributaries and karst springs with low proportions of forested LCA demonstrated low concentrations of nutrients and ions, such as a few tributaries in LACS, we presume they may be subjected to a legacy effect where water quality may decline with minimal land use change in the future. This challenge of not being able to delineate true boundaries of a catchment in karst landscapes nor knowing the age of the contributing waters may explain the lack of significant relationships between land use and nutrients in the mainstems.

In addition to agriculture, other sources may be affecting water quality, such as wastewater. Wastewater was found to be a dominant source of  $\text{NO}_3\text{-N}$  across all sites and, specifically, in the mainstem, during the fall, and in karst springs in spring 2016,



based on the significant findings between  $\text{NO}_3\text{-N}$  and  $\text{Cl}^-$  (Chen et al. 2017, Adimalla 2020). High levels of  $\text{Cl}^-$  is often attributed to road salt, but treated wastewater, water conditioning salts, synthetic fertilizer (KCl), and livestock waste can also be sources (Kelly et al. 2010). Road salt usually increases with urbanization and is highest in the winter and spring (Kelly et al. 2010). The major land use of these subwatersheds are forest and agriculture where the highest mean concentration was during fall sampling ( $\bar{x}$ =17 mg/L; spring samples:  $\bar{x}$ =14.9 and 14.2 in 2016 and 2017, respectively). However, this was similar to the concentrations found by Morgan et al. (2007) in Maryland streams with 0–9.9% urbanization ( $\bar{x}$ =16) where  $\text{Cl}^-$  was attributed to road salt, yet no other sources were considered. The mean of karst springs for the spring 2016 sampling was lower at 9.9 mg/L and ranged from 1.9–27 mg/L. Sources can be further identified using the Cl:Br ratio but is not a reliable method due to the large overlap among the different sources. It can thus be used in conjunction with other techniques to serve as further validation.

The Cl:Br ratios found in some of the sites during the fall sampling season and karst springs during spring 2016 indicate contamination from multiple sources. The mean ratio of all sites together was 1112 and the mainstem was 1073. Sites ranged from 148 to 3864 and mainstem only ranged from 298 to 2733. The Cl:Br ratio of wastewater has been shown to range from 300 to 600 for septic effluent, indicating only a few of the sites may have been contaminated by leaking septic systems (Panno et al. 2005). A potential source explaining the higher ratios is road salt or fertilizer. In England, urban runoff contaminated by winter road salt had a mean ratio of 1167 (Davis et al. 1998) and in Chicago, stream waters in February had ratios as high as 14,000 (Panno et al. 2005).

However, groundwater can continue to be contaminated from road salt year round at lower concentrations from dilution (Kelly et al. 2010), which is a scenario that can likely affect concentrations from other sources as well. Waters found to be affected by KCl had Cl:Br ratios from 108 to 1974 (Panno et al. 2005), which can also explain some of the higher ratios found in the mainstem, especially those also high in  $K^+$ . The karst springs showed supportive evidence of septic effluent with a mean ratio 591 but several sites exceeded the 600 Cl:Br ratio with a range of 170–1007. Ranges of other potential sources include 86–146 for cattle, horses, and goats (Hudack 2003), 1245–1654 for horses and hogs; and 90–140 from granite and metamorphic rocks (Davis et al. 1998). Although the ratios did not provide sufficient support for wastewater contamination, we can assume that the sites with elevated  $NO_3-N$  concentrations is either from agriculture or failed septic systems. High bacterial levels attributed to failed septic systems and animal waste in Antietam Creek have recently become a public concern (McMillion 2020). In 2015, \$14 million was approved to provide funding for septic system upgrades throughout rural areas in Maryland, including Washington County, that would reduce N pollution by at least half (Lovelace 2015). Therefore, several mitigation practices are being implemented to address contamination from various sources that are affecting the water quality of these streams.

BC subwatershed showed evidence of fertilizer during both spring sampling seasons. A major contributor to its water quality is the major karst spring feeding the Albert Powell Hatchery where the BC mainstem changed in constituent concentrations instantly in response to the spring contribution around ~50 km TCA (Fig. 3.3). Investigations on the contributing waters of the karst spring has shown sources from

neighboring subwatersheds, including LACN's using dye tracers discharge measurements, that is controlled by faults and may change depending on groundwater levels. Nutrient concentrations from 2008 were low except for NO<sub>3</sub>-N (i.e., NH<sub>4</sub>-N: <0.02; NO<sub>3</sub>-N: 6.08; PO<sub>4</sub>-P: 0.013 all in mg/L) (Duigon 2009). The range of nutrient concentrations we found from the spring discharge into Beaver Creek in mg/L were: 0.12– 0.18 for NH<sub>4</sub>-N; 3.8 – 5.1 for NO<sub>3</sub>-N; consistently 0.02 for PO<sub>4</sub>-P). NH<sub>4</sub>-N was low throughout the BC mainstem with a slight increase after merging with the hatchery discharge. However, concentrations returned back to pre-hatchery levels at a site about 10 km downstream. NO<sub>3</sub>-N concentrations also increased from the hatchery and continued to increase until the final outlet site. Two tributaries further downstream also had high levels of NO<sub>3</sub>-N albeit lower than the mainstem's before the tributary-mainstem confluences, but still may have assisted with maintaining high concentrations.

Is there any evidence of nutrient retention in these streams? Stable isotopes of nitrate ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$ ) demonstrated the mixing of tributaries and karst springs with the mainstem further supporting our hypothesis that water quality of the mainstem ultimately depends on the major contributing waters (Appendix M–P). However, isotopes also indicated evidence of denitrification in all of the mainstems from anecdotal observation of the  $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{NO}_3}$  and NO<sub>3</sub>-N relationships that showed fractionation—possibly within the catchment or from microbiological activity within the streambed (Triska et al. 1989, Cirimo and McDonnell 1997, Mulholland and Hill 1997, Butturini and Sabater 1999, Grimaldi and Chaplot 2000, Hinkle et al. 2001, Hall et al. 2002, Ruehl et al. 2007).

Isotope data from the samples collected during the spring season showed denitrification in response to FEHA (LACN & LACS), albeit concentrations of  $\text{NO}_3\text{-N}$  exhibited no response to FEHA (Appendices E,F,I,J). During the fall season, majority of the significant correlations between planted forest buffers/FEHA and nutrients were found, which is also when discharge rates were the lowest (Fig. 3.4). Denitrification along the streambed is more efficient when discharge rates are low (Ruehl et al. 2007) and, according to one study, denitrification was found to remove 75% of  $\text{NO}_3^-$  during the fall season (Dhont et al. 2003). The presence of riparian vegetation can create environments more conducive to denitrification and other microbial processes by supplying mineralizable sources of organic carbon from leaf litter, root decay, and root exudates (Cooper 1990, Haycock and Pinay 1993, Broadmeadow and Nisbet 2004, Parkyn 2004). Unfortunately, only one sample was tested from each site, and none were from the fall sampling date that could otherwise help explain the primary mechanism for these nutrient declines. However, without the subtle decline of N in the mainstem, whether it is from denitrification or retention from riparian forest buffers and FEHA, we can assume the final outlet site would be much higher without the presence of riparian forest regions supporting these biological processes.

In an effort to model nutrient discharge in karst landscapes, we developed and tested two models, where one incorporated catchment area and the other used actual discharge. Overall, we found the “actual flow model” worked best based on NSE and RMSE, but this depended on the watershed and the constituent being modeled. BC concentrations were the most difficult to predict because reaches were sometimes dry along the mainstem or was a losing reach, making the actual measured discharge

necessary when predicting nutrient concentrations. The “base model” predicted  $C_{lat}$  variations in LACN and LACS best where the majority of the mainstem contained gaining reaches and had consistently, large contributions from lateral groundwater. Therefore, the accuracy of the model most-likely depends on the hydrology of the watershed. TDN and TDP were more challenging to model because they can convert into different chemical forms depending on the environment and susceptibility to biological uptake. For instance, the “actual flow model” was optimal for majority of the MB constituents except for TDN in the fall season where the “base model” was optimal. Nonetheless, the mainstem contained little contribution from net lateral inflow during this season.

Based on the NSE values and the Pearson’s Chi-square test, the models did not do an overwhelmingly better job at predicting less biologically reactive constituents over N and P. The only significant differences were between the subwatersheds. Therefore, no matter what the constituent (less biologically reactive or not), it is difficult to predict nutrient and ion concentrations of streams located in the R&V because of the inherent hydrogeological complexity. Early modelers have found the same issue when applying hydrological theories to models to explain karst aquifers. In most instances, springs and fractured conduits are ignored (White 2002). We suspect the “actual flow model” captures some of these anomalies and incorporates it into its calculations, thus making it the superior model.

Although no significant results were found using one-way ANCOVA to control for geology (bedrock present at site), presence/absence of faults, and presence/absence of karst there is reason to believe from our results and other studies that geology affects the

stream chemistry (Miller et al. 1997, Liu et al. 2000, Eshleman and Sabo 2016) and the function of riparian forest buffers. Our study sites did not have equal populations under each covariate to test whether these controls affect riparian buffer function, and we attribute this to our lack of significant findings.

The range of N concentrations found within these subwatersheds are generally low compared to the Coastal Plain where  $\text{NO}_3\text{-N}$  concentrations typically exceed 10 mg/L in groundwater below agricultural lands (Denver et al. 2014). Nevertheless, TN loads of the Potomac River have increased 215% over the last century mainly from agriculture. The Potomac River basin is the second largest contributor of nitrogen to the Chesapeake Bay (EPA 2010, Lookingbill et al. 2009, Boyer et al. 2002). However, in 2019, USGS found total nitrogen and phosphorus loads to be improving in the four largest tributaries of the Bay, including the Potomac River (Moyer and Blomquist 2020). Much of this success can be attributed to Maryland's Phase I & II Watershed Implementation Plan (WIP) that includes riparian buffer plantings (US EPA 2020). The EPA recently created new pollution reduction targets of 22 million kg of N per year for the Potomac River by 2025. In 2018, USGS estimated 20 million kg of N are being reduced indicating goals may be reached before the set deadline (Potomac Conservancy 2020). Evidence of nutrient decline indicates riparian forested buffers are working in some capacity within the Potomac River watershed. By combining data sets from this study and Chapter 2, we found TDN load retention rates between 6.4 and 64.2 kg/ha-yr with 100% forested buffer areas, which includes mature, natural forest and recently planted buffers. Although, several outliers were removed, we can assume that some riparian buffers implemented in the R&V can reduce nutrients from surface waters;

however, more research is needed on what characteristics and mechanisms are most critical to their function.

### ***3.6 Conclusion***

While we found some negative correlations with nutrients and land use, our goal was to investigate the success of riparian forest buffers in reducing nutrients across karst regions. We did not see clear evidence supporting riparian forest buffers as a means of mitigating nutrients within these subwatersheds, suggesting hydrogeomorphology to be a critical factor in limiting their success. Our study showed most nutrient reduction in response to an increase in canopy and FEHA (forested riparian area that included mature forest and newly planted buffers), and possibly from in-stream processing. If riparian forest buffers are managed properly, we suspect they will eventually perform similarly to the mature riparian forest. This would require reforestation of riparian areas beyond the 10- to 15- year Conservation Reserve Enhancement Program contracts. Our results also concluded that stream water quality relies heavily on its major contributors (i.e., groundwater, tributaries, and karst springs), but the predominant sources can change on a short temporal scale. The recharge location of some of these contributors (i.e., karst springs) are also often unknown; therefore, to improve stream water quality throughout this region not only requires protecting the riparian area and land use within that specific catchment, but its surrounding watersheds as well.

### ***3.7 Acknowledgements***

We thank the Maryland Department of Natural Resources for allowing us access to their Conservation Reserve Enhancement Program files to determine location of

planted buffers and for their assistance with the study. We thank Nathan Reinhart for his assistance in digitizing all of the planted CREP riparian buffers in ArcGIS and Jim Garlitz, Joseph Acord, Briana Rice, Robin Paulman, Joel Bostic, and Jacob Hagedorn for helping to collect, run, and analyze water samples. This research was supported by a USGS competitive grant through the Maryland Water Resources Research Center.



## Chapter 4: Costs and benefits of reducing nutrients from riparian buffers in western Maryland

### **4.1** *Abstract*

This paper estimates the economic cost of nutrient reduction from riparian buffers to improve water quality in the Ridge and Valley (R&V) physiographic province in western Maryland. First, we conducted a benefit-cost analysis (BCA) to evaluate the potential economic gains landowners receive for implementing riparian buffers under the Conservation Reserve Enhancement Program (CREP) in Allegany and Washington Counties. We evaluated three scenarios: (1) converting cropland to a riparian grass buffer, (2) converting cropland to a riparian forest buffer, and (3) establishing riparian forest buffers next to a pre-existing natural forest along a stream. BCA results were used to estimate the economic cost of nitrogen and phosphorus reductions under these three scenarios. We estimated nutrient reductions using the Chesapeake Bay Watershed Model and our data from a synoptic study. Results show the cost-effectiveness of nutrient reduction can be achieved by implementing a specific riparian buffer practice but varies based on spatial location and pollutant. According to our analysis, converting cropland to a grass buffer is the least costly practice for reducing nitrogen and phosphorus in western Maryland but converting cropland to a riparian forest buffer is the most beneficial CREP practice to landowners based on economic gains. The conversion of cropland to a riparian forest buffer next to a natural forest can reduce a moderate amount of nitrogen but it varies based on certain circumstances. Nutrient reduction rates using our two models highlight the uncertainty of buffer function within the R&V.

## **4.2 Introduction**

The Chesapeake Bay watershed (CBW) is home to over 18 million people (Chesapeake Bay Program 2019a) and supports an immense amount of economic activity (e.g., agricultural, industrial, and municipal). This activity has negatively affected the Chesapeake Bay's water quality (Wainger et al. 2013), where signs of major water quality degradation began in the 1970s after a population boom (Chesapeake Bay Program 2019a). Since then, multiple strategies have been implemented to improve the Bay's health, focusing specifically on mitigating nutrients from agriculture.

One strategy is the implementation of riparian buffers, where current research supports their use as a best management practice (BMP) (Sutton et al. 2009). This has led to the establishment of cost-share programs, such as the Conservation Reserve Enhancement Program (CREP) — an annex of the Conservation Reserve Program (USDA and FSA 2018) — that promotes riparian buffers by offering pecuniary support for their establishment and maintenance. Research has found that riparian buffers improve water quality by reducing stream sedimentation and nutrient (nitrogen/phosphorus) runoff from cropland (Bonham et al. 2006) by filtering nutrient rich surface and subsurface waters that flow from agricultural fields into adjacent waterways. On the state level, Maryland CREP is a central mechanism for motivating cropland owners (i.e., producers) to convert a parcel of agricultural land to a riparian buffer (e.g., forest, wetland, or grassed streamside) for a 10–15-year period (Maryland Department of Natural Resources 2019a). Those eligible to enroll must either own or have operated the farm one year prior to enrollment; have erodible land within 305 m of a stream or cropland bordering a body of water that meets farming history requirements;

and currently be physically and legally capable of being planted. Marginal pastureland is also eligible for certain practices (USDA- NRCS 2014).

In 1997, Maryland became the first state to participate in CREP and pledged to implement 40,500 ha into the program to reduce 5.2 million kilograms of nitrogen, 0.5 million kilogram of phosphorus, and 200,000 tons of sediment annually to achieve water quality goals in the Chesapeake Bay (Maryland Department of Agriculture 2017). Almost half of the counties in Maryland have buffered, or partially buffered, 85% of their streams. In Allegany and Washington Counties, about 75% and 41% of streams are fully buffered with, over the last decade, an average of 10 ha of riparian buffers planted per year across the two counties (J. Winters/ DNR 2018, J. Winters 2018a, J. Winters 2018b). Other counties have less percentage of streams buffered, impeding Maryland from reaching its goal — about 27,000 ha are enrolled under MD CREP (Noto 2015) and, according to 2019 data, only about 11,000 ha are forest buffers (Maryland Department of Natural Resources 2019b).

In the state of Maryland, between 2010 and 2017, about 35 km of forest buffers on average were planted annually along rivers and streams, reaching only 29 percent of the restoration target since 2010 (Chesapeake Bay Program 2019b). In 2019, fewer than ten km of riparian buffers were planted in Maryland — the lowest restoration in the last 22 years (Chesapeake Bay Program 2019b, Maryland Department of Natural Resources 2019b). Several factors contribute to CREP's declining enrollment including delays and closures of the program, reluctance to remove cropland out of production, insufficient economic incentives to producers, lack of flexibility and funding through federal programs, re-enrollment issues and expiring contracts, and lack of outreach (Vetter 2018,

Chesapeake Bay Program 2019c). Moreover, about 10–30% of existing riparian buffer ha will expire under CREP in the next five years (Noto 2015).

While federal and state agencies aim to increase riparian buffers and preserve those existing, focus should also be on how to exploit funds most efficiently, since resources and incentives are limited. Efforts towards increasing enrollment should be prioritized where benefits exceed costs by installing buffers where they will function optimally. Our main objective is to quantify the economic cost of potential nutrient reduction in streams from riparian buffers in the Ridge & Valley (R&V) portion of the CBW in western Maryland. Our second objective is to evaluate economic net gains from riparian buffer installation and determine the cost-effective practice of a riparian buffer to improve stream water quality. Cost savings could be achieved through selections of riparian buffer restoration practices based on nutrient mitigation. These objectives are relevant to water quality improvements in streams through the reduction in nitrogen and phosphorus and to the development of the economic approach for the cost estimation in nutrient mitigation from riparian buffer restoration on agricultural land.

Few studies have conducted economic analyses on riparian buffer restoration. In particular, cost and benefit estimations of establishing riparian buffers on agricultural land in different regions under CREP have been evaluated by Nakao et al. (1999) and Nakao and Sohngen (2000), Lynch and Tjaden (2000), Wossink and Osmond (2002), among others. A limited number of recent studies has focused on buffer-water-related economic costs of nutrient mitigation (Bonham et al. 2006, Wieland et al. 2009, Shortle et al. 2013, Kaufman et al. 2014). Specifically, Bonham et al. (2006) assessed the compliance costs and reductions in phosphorus from implementation of nutrient

management and riparian buffers under CREP. Wieland et al. (2009) developed cost estimates and summarized cost efficiencies for nutrient mitigation BMPs, including for riparian buffers of the Chesapeake Bay. Shortle et al. (2013) and Kaufman et al. (2014) investigated the economic impacts from reducing nutrient discharge through credit trading programs and estimated costs to agricultural producers of the Watershed Implementation Plans (WIPs) developed by states in the Chesapeake Bay Watershed. In particular, Wieland et al. (2009) estimated average establishment CREP costs of riparian buffers in the range of \$931 to \$2,400 per ha and the corresponding nitrogen reduction efficiencies across 9 geographic regions/provinces and geological types. Shortle et al. (2013) estimated the cost of removing pollutants from implementing agricultural BMPs under a nutrient credit trading scenario in the range from \$4.4 to \$44 per kg of nitrogen and \$22 to \$220.5 per kg of phosphorous in 2010 dollars. However, buffers were not included in their cost analysis of nutrient reductions due to data limitations. We recognize that buffers have multiple benefits other than nutrient mitigation, such as providing a natural habitat for wildlife, stabilizing stream banks, controlling stream temperature, and supporting aquatic ecosystems, among others. However, in this paper, our main focus is on the economic assessment of riparian buffers for the improvement of stream water quality from nutrient mitigation.

We used the Chesapeake Bay Watershed Model (CBWM) to estimate nutrient reduction from riparian buffers within the streams of western Maryland, (Chesapeake Bay Program 2019d). The CBWM estimates the amount of nitrogen, phosphorus, and sediment pollution reaching the Chesapeake Bay, which is used by USEPA and other agencies at the federal, state, and local levels. The current version 6 of the model

simulates nutrient reductions from forest and grass buffers based on their nutrient efficiency loads determined for each hydrogeomorphic region. However, various studies suggest that efficiencies for riparian buffers are specific to the geographic and watershed conditions. The function of a buffer generally relies on the hydrological components of the catchment, such as water table depth and subsurface flowpath. The CBW stretches across several physiographic provinces (Lowrance et al. 1997), where only a few studies have investigated riparian buffer function in the R&V (Weller et al. 2011, Schnabel et al. 1997). These studies indicate uncertainty and variability in nutrient reductions because of the heterogeneity of the landscape from the karst-terrain that affects near-stream hydrology. Therefore, we also utilized empirical estimates from a self-conducted synoptic study of riparian buffer function (Chapters 2 & 3) of 76 reaches throughout Allegany and Washington Counties of western Maryland during the 2014–2017 period. The empirical study included riparian forests planted under CREP and older naturally-established forests because data did not show strong indication of nutrient reduction using recently planted riparian forests alone. We assume that once planted trees mature, they would function similarly to the mature riparian forests if managed properly. This is supported by findings of Bradburn et al. (2010) who found inadequate survival of trees planted through CREP and a slow regeneration rate of natural vegetation within the R&V. Using this data on nutrient mitigation from riparian buffers, we conducted an economic assessment of establishing riparian buffers under CREP and estimated the costs of the potential nutrient reductions. The results could be used by managers to compare costs for establishing different types of buffers in the region, while considering their cost-effectiveness with respect to nutrient reduction. Study findings could also encourage

longer contract periods that may be required to allow riparian buffers to mature and become functional.

### ***4.3 Study region***

The Ridge & Valley (R&V) within the Appalachian Mountain region makes up 53,120 km<sup>2</sup> (32%) of the Chesapeake Bay's watershed (CBW). The geology comprises adamantine ridge capstones, including siliceous sandstone and conglomerates. The deeper bedrock and valley bottoms are limestone and shale that easily erodes through chemical dissolution and fluvial processes (Fenneman 1938, Lowrance et al. 1997). In some areas, extensive erosion has led to the formation of karst terrain, including a network of unmapped caverns and caves that enhances hydraulic conductivity and produces many springs and seeps (Grumet 2000). Because of this unique mountainous terrain, only a few studies have estimated the function of riparian buffers, and, to our knowledge, no study has done a benefit-cost analysis (BCA) of riparian buffers implemented through CREP nor estimated the economic value of nutrient retention in this region. As a result, we selected two western Maryland counties, Allegany and Washington within the R&V.

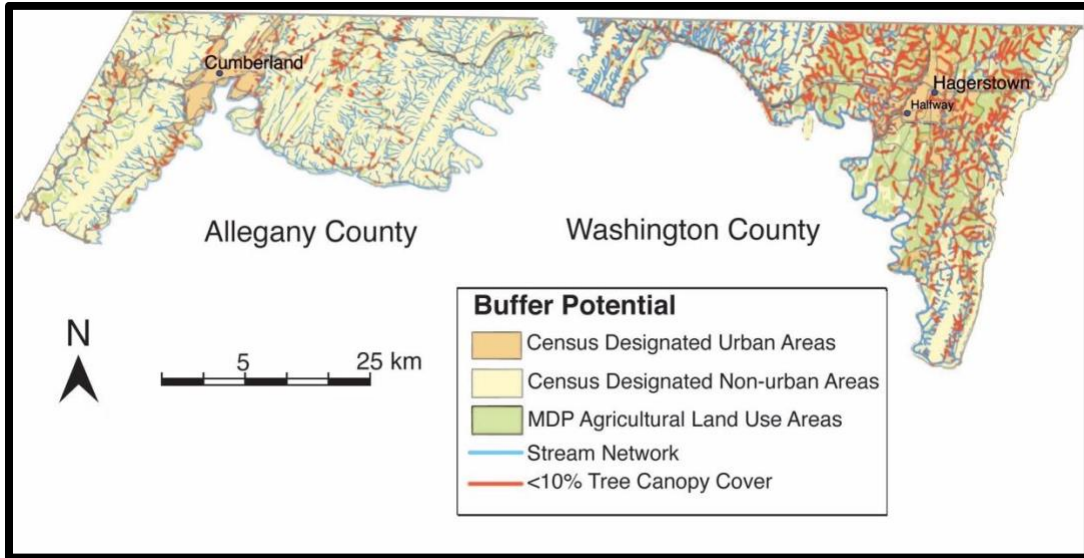


Figure 4.1 Distribution of riparian forest buffer locations along the streams in Allegany and Washington Counties based on 2013/2014 high resolution landcover dataset from the Chesapeake Bay Conservancy. (Reproduced using figures from J. Winters 2018a and J. Winters 2018b.)

Figure 4.1 shows the spatial distribution of streams in Allegany and Washington Counties where riparian buffers could be implemented. The red lines indicate less than ten percent of tree canopy cover (buffer potential) and green areas represent the agricultural land use areas. The potential agricultural area where riparian buffers could be established is estimated at 346 ha (854 acres) in Washington County and 76 ha (188 acres) in Allegany County (Figure 4.1, Table 4.1) (Winters 2018a, 2018b).



Table 4.1 Riparian Buffers in western Maryland\* and the State of Maryland.

<b>Region</b>	<b>Percent of Existing Buffers (%)**</b>	<b>Existing unbuffered (acres)</b>	<b>Agricultural Buffer Potential (acres)</b>
Allegany County	75	418	188
Washington County	41	2,400	854
Western MD	61	3,823	ND
Maryland	57	18,790	ND

*Data from DNR, 2018*

*Notes:* \* Western Maryland includes Allegany and Washington Counties, as well as Garrett County within the Chesapeake Bay Watershed.

\*\**Buffers refers to buffers that are at least 100 feet (30.5 m) wide.*

*ND=no data*

## **4.4 Methodology**

### **4.4.1 Riparian buffer scenarios and nutrient reduction**

We used three different scenarios (Fig. 4.2) to perform an economic analysis on riparian buffer installation: (1) conversion of one acre of cropland to a streamside grass buffer (Fig. 4.2A), (2) conversion of one acre of cropland to a streamside riparian forest buffer (Fig. 4.2B), and (3) enhancing a riparian forest area by converting ½ an acre of cropland to a riparian forest buffer next to ½ an acre of a pre-existing natural forest, summing to a full 1 acre of forest along the stream (Fig. 4.2C). (Note: 1 acre = 0.4 ha and is the standard measurement of area used under CREP). We modeled the riparian grass buffer scenario after conservation practice (CP)-21(i.e., grass filter strip) under CREP, where grass filter strips must be at least 10 m wide next to a perennial or seasonal stream. We modeled the forest buffer scenario after CP-22 under CREP. This includes a strip of trees with a width between 10 to 30.5 m, bordering a perennial or seasonal stream or a waterbody. The last scenario includes the combination of a planted riparian forest buffer next to a natural forest that is bordering a perennial or seasonal stream with a width of up

to 10 m. Since this incorporates natural mature and young forest, in addition to plantings under CREP, from hereafter it will be referred to as ‘unclassified forest buffer.’

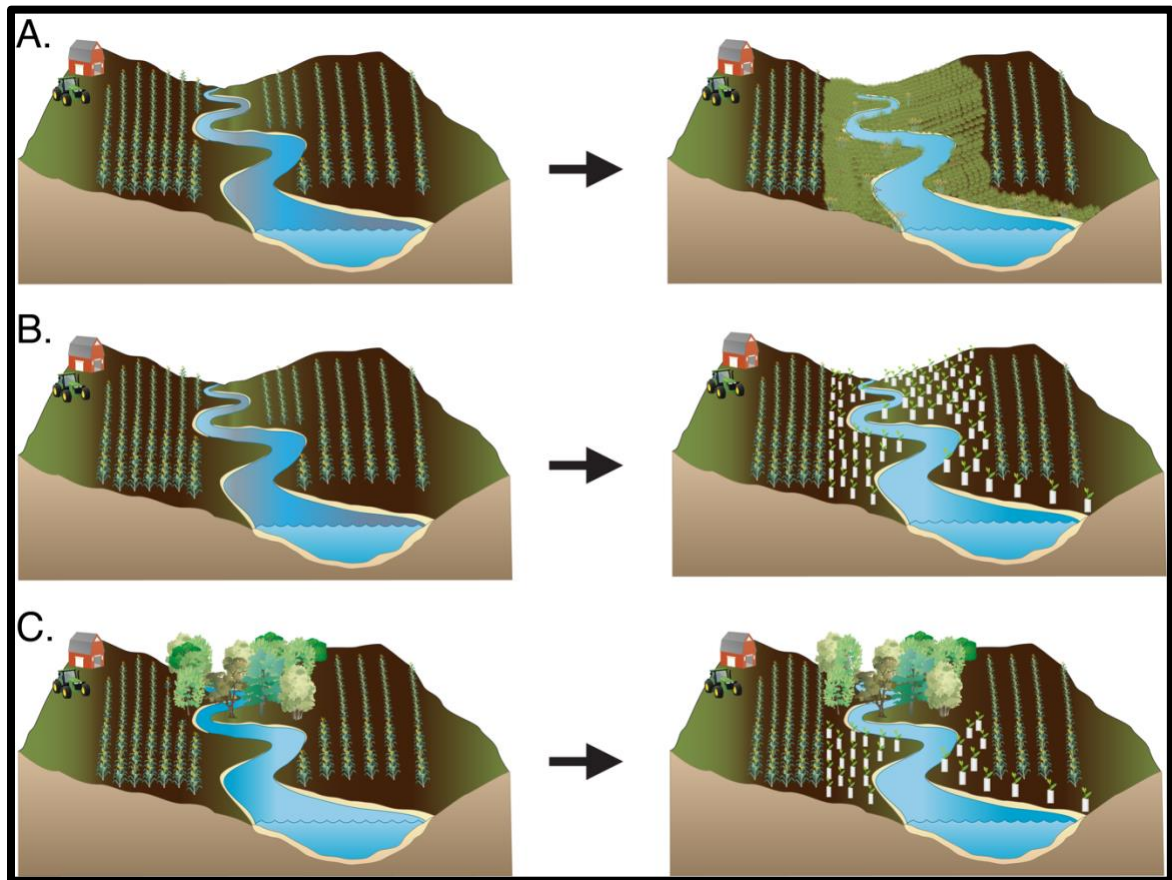


Figure 4.2 Conceptual diagram showing the three scenarios of buffer installation for the economic analysis. Scenario (A) illustrates conversion of cropland to a riparian grass filter strips; (B) illustrates a conversion of cropland to a riparian forest buffer with protective tree shelters to reduce deer browsing; and (C) illustrates the last scenario of an unclassified buffer where a natural, pre-existing buffer is enhanced by converting  $\frac{1}{2}$  of a cropland area to a riparian forest buffer to equal one acre of forest buffer.

### *Nutrient reduction*

We obtained the nitrogen and phosphorus reduction estimates from the Chesapeake Bay Watershed Model (CBWM)-Phase 6. The data from CBWM represent loads of nitrogen and phosphorus that are reduced by the implementation per unit or acre of BMP on the county level. We accounted for annual kilograms of nitrogen and

phosphorus reduced per acre for establishing grass or forest buffers in Allegany and Washington Counties (Table 4.2). The nutrient reductions represent typical amounts of nutrients reduced at the edge of the stream area which have been estimated using the Chesapeake Assessment Scenario Tool (Chesapeake Bay Program 2019d).

The CBWM simulates load reductions for different types of buffers and applies different efficiency of pollutants removed per BMP, including grass buffers, grass buffer-streamside with exclusion fencing, forest buffers, and forest buffer-streamside with exclusion fencing. The load reductions consider the conversion of land use, such that if the land is converted from cropland (high nutrient sources) to a riparian buffer (low nutrient source) then this will automatically decrease nutrient loads. In circumstances where the riparian buffer protects an area larger than itself, one needs to adjust the simulated load reduction to account for the area protected from the riparian buffer. For example, according to the CBWM, nitrogen reduction for every one-acre of forest buffer of 10 m is assumed to cover two acres of upland and two acres of adjacent land (Chesapeake Bay Program 2019d). In this case, the nitrogen reduction from establishing a buffer was multiplied by a factor of four. For phosphorus reduction, the efficiency of a riparian buffer is twice the amount reported on agricultural land and was multiplied by a factor of two. These different efficiency factors are based on the literature reviews used to create the model that indicate buffers can effectively reduce nitrogen in surface and subsurface flows, but phosphorus retention is more dependent on sediment and surface flow (Simpson and Weammert 2009). We summarized the range of nutrient reductions for establishing a riparian buffer in Allegany and Washington Counties based on CBWM results as of 2019 (Table 4.2). Because the actual reduction in nutrients depends, in part,

on whether buffers treat agricultural land of high-nutrient loading compared to areas with low nutrient loading, the range of nutrient reduction is widespread.

Using the experimental data from Chapter 3 with the combined data sets from Chapter 2, we found TDN load retention rates for sites containing 100% forested riparian areas. Both studies were conducted in the R&V in Allegany and Washington Counties during baseflow conditions and sites were a combination of planted buffers and naturally forested riparian areas. Planted forest buffers alone showed no significant declines in nitrogen nor phosphorus; however, sites combining naturally forested riparian areas with planted riparian forest buffers achieved significant nitrogen reductions. We assumed for the purpose of this analysis that the planted forests behave the same as the natural mature forest and developed a simple linear regression model to predict reductions of TDN loads in net lateral groundwater ( $F(1,74)=18.03$ ,  $p\text{-value}=6.2E-05$ ;  $R^2=0.2$ ;  $n=76$ ) (Fig. 3.6, Chapter 3). Using this model, we predicted maximum reduction of TDN loads for each of our 76 sites by finding the difference between nutrient loads when sites are fully buffered (100% riparian forested area) and when lacking a riparian buffer (0% riparian forest). Loads were calculated by multiplying the concentrations by each site's measured net lateral groundwater discharge ( $\text{m}^3 \text{s}^{-1}$ ). Loads were converted to  $\text{kg/ha-yr}$  by dividing by the total riparian area of each site. Loads were converted to  $\text{kg/acre-yr}$  to allow a direct comparison with the CBWM results.

We calculated 95% prediction intervals of the intercept (lower bound: 0.2 and upper bound: 3.9  $\text{mg/L}$ ) to find a range of TDN reduction loads that would best capture the variation of nutrient reductions when establishing a riparian buffer along a random reach within the R&V. The concentrations found using the linear regression model were

again multiplied by each site's net lateral groundwater discharge and their medians were used to define the minimum and maximum loads. Based on USGS stream gauge data, the median discharge rate was very similar to the mean long-term runoff rate of Town Creek watershed — the watershed in which many of our study sites are located (U.S. Geological Survey 2021). Using this comparison as validation, we moved forward by using the median found by Microsoft Excel's Descriptive Statistics Tool (2021) of the computed instantaneous nutrient loads to represent annual riparian buffer nutrient reduction. Combing sites from both chapters did not produce a significant correlation between TDP and percent riparian forest buffer, even after several outliers were removed. Additional information on data and the model can be found in Chapters 2 and 3.

Table 4.2 Nutrient Reduction Loads

Nutrients/County	Grass Buffer**†	Forest Buffer*†	Forest Buffer - Narrow***†	Unclassified Forest Buffer‡
<i>Allegany County, MD:</i>				
Nitrogen, kg reduced per acre per year	9.9–53.3	12.6–56.1	16.0	2.6–25.8
Phosphorus, kg reduced per acre per year	0.04–16.0	0.21–16.2	4.6	0
<i>Washington County, MD:</i>				
Nitrogen, kg reduced per acre per year	14.1–123.7	17.6–126.5	36.2	2.6–25.8
Phosphorus, kg reduced per acre per year	0.1–27.0	0.2–27.0	7.7	0

Note: \*The lower bound shows the loads of nutrients reduction for grass or forest buffer. The upper bound shows the loads reduction for grass buffer-streamside or forest buffer-streamside with exclusion fencing.

\*\* Forest Buffer Narrow with exclusion fencing. Narrow buffer width is between 10 and 34 feet.

†Estimates from CBWM (2019) for total nitrogen (TN) and phosphorus (TP).

‡Estimates from Chapters 2 & 3 incorporating natural and planted riparian forests. Nitrogen measurements includes total dissolved nitrogen (TDN) only.

The overall prospective reduction of nutrients varies among buffer type with some variation across the counties (Table 4.2). The CBWM shows that each acre of grass buffer reduces nitrogen in the range of 9.9 to 53.3 kg in Allegany County, and 14.1 to 123.7 kg in Washington County per year. Similarly, each acre of forest buffer is likely to reduce nitrogen in the range from 12.6 to 56.1 kg per year in Allegany County, and 17.6 to 126.5 kg per year in Washington County. Grass buffers are estimated to retain 0.4 to 16.0 kg of phosphorus per year in Allegany County, and 0.09 to 26.9 kg per year in

Washington County, while forest buffers are expected to reduce about 0.21 to 16.2 kg of phosphorus in Allegany County, and 0.2 to 27.0 kg of phosphorus per year in Washington County. These values from the model do not directly account for upgradient or adjacent land use to the buffer, but it does apply the efficiency proportionally to agricultural land uses in a land-river segment.

For comparison, we also considered nutrient reduction for narrow forest buffers (width between 3 to 10 m) on agricultural land. The values for nutrient retention for narrow forest buffers are about 3.5 times lower than those reported for similar types of forest buffers with a width of 30.5 m. Note, Sweeney and Newbold (2014) found that among the 30 studies reporting buffer width, water flux, and vegetation, the removal efficiency of nutrients was not significantly correlated with buffer width.

In our last scenario using our empirical data, an acre of the unclassified forest buffer was found to reduce nitrogen within a range of 2.6 to 25.8 kg per year based on the upper and lower bound of the 95% prediction interval in Allegany County and Washington County (Chapters 2 & 3) (Table 4.2). These loads are within the ranges found using the CBWM to estimate nitrogen reductions. However, the maximum amount predicted by CBWM is two times higher than our model predicted in Allegany County and almost five times higher in Washington County. One possible difference is our reduction loads were calculated by multiplying the stream discharge rates with the measured nutrient concentrations from stream water samples collected during baseflow conditions in the spring and fall. We extrapolated our data to represent an annual reduction, but our study only considers nutrient retention in groundwater in two seasons, and we only measured dissolved concentrations of nitrogen where the majority of N was

nitrate (NO<sub>3</sub>-N). CBWM rates were based on surface and subsurface retention of nitrogen (total N), and their nutrient retention rates are not reflective of the variability found across the landscapes. The high retention rates in the CBWM are also based on high nutrient loads (Simpson and Weammert 2009), where we did not measure the nutrient loads in the upland groundwater in our study sites. The CBWM also provides retention rates of phosphorus, but our sites did not demonstrate a significant relationship. Our study was conducted during baseflow conditions and only tested soluble forms of P. The most common forms in cropland are bound to soil particles that are released during storm events (Liu et al. 2000), which we did not sample.

#### **4.4.2 Estimating economic costs and gains of riparian buffers**

##### *Economic assumptions*

The general background and economic assumptions have been considered associated with installing a riparian buffer. For the analysis, we used the cost-benefits analyzing tool entitled "\$Buffer" (Bentrup 2007) and self-constructed spreadsheets along with the CREP Maryland Chesapeake Bay factsheet as of April 2018 (Farm Service Agency 2018). Under the three hypothetical scenarios, we assessed the conversion of one acre of cropland to a streamside filter strip or grass buffer; conversion of one acre of cropland to a riparian forested buffer; and conversion of ½ an acre of cropland to a riparian forest buffer adjacent to another ½ an acre of natural forests, summing to a full 1 acre of riparian forested area along the stream. CREP enrollment is only considered for areas adjacent to a stream or waterway or located within 305 m of a stream. Because a naturally forested riparian region along a stream typically cannot be enrolled into CREP, only acreage converted to a riparian buffer is accounted for potential incentives. The



period of conversion is assumed to be 15 years — an average period of a typical CREP contract.

Based on the three scenarios, we estimated the economic costs and gains of buffers using CREP in Allegany and Washington Counties within the R&V Province. To calculate total economic costs of establishing riparian buffers, we used information about average costs for planting and establishing a buffer and annual maintenance costs in Maryland from USDA for 2019. All costs were estimated on a per acre basis without fencing; however, we included the protective tree shelters for the riparian forest buffer plantings because it is a standard practice to protect sapling trees from deer in western Maryland. The costs for establishing riparian buffers include installation costs, continuous maintenance and mowing costs, and opportunity cost in the form of lost income to producers. The latter represents the value of foregone income from the removal of cropland from production. The economic gains to producers include rental payments and incentives from CREP that producers gain from cropland conversion into a riparian buffer, and cost-sharing assistance for establishing vegetative cover or implementing conservation practices. Rental payments and incentives were based on the average soil quality of cropland for each county. These benefits may offset the costs to producers; however, the program payments, along with other bonuses, and technical assistance are paid by the government, so that these payments reflect public expenses to establish riparian buffers.

#### *Economic analysis*

To express relationships between resource quality and land conversion, we used a model to examine the resource and the economic value of its use (Freeman 2003). Let  $q$

represent the environmental resource (land, water, etc.) quality and  $S$  represent the government regulation designed to remove the land from agricultural production and convert it to a riparian buffer (forest or grass), such that  $q(S)$  represent the changes in  $S$  on  $q$  that affects the private decision-making. Because private response depends on the governmental regulation,  $R(S)$ , the function of  $q$  on government regulation and private responses to the regulation is given as:

$$q = q[S, R(S)]. \quad (1)$$

The private decision to convert land to a riparian buffer depends on private costs for establishing a conservation practice,  $C_t(q)$  and producer benefits or gains  $B_t(q)$  received from the conservation program. The costs and benefits are flows of money over time  $t$  during the length of the contract,  $T$ . In some cases, the producer's benefits also include additional income from harvesting trees, hunting, and/or fishing, but these activities are not considered in this analysis.

The net present value (NPV) of net benefits to producers at time  $t$  can be expressed as:

$$NPV = \int_0^T [B_t(q) - C_t(q)] e^{-rt} \quad (2)$$

where the term  $e^{-rt}$  discounts the future streams of net benefits at the discount rate  $r$  over time  $t$ . The economic costs  $C_t(q)$  to producers are sum of initial establishment cost to convert the land and install a buffer in initial period  $t = 0$ , defined as  $C_o(q)$ , maintenance cost  $M_t(q)$  at time  $t$ , and land opportunity cost or foregone income, given as  $O_t(q)$ .

Gains to producers are sum of annual rental payments under the conservation program based on soil quality in the form of average soil rental rate,  $R_t(q)$ , one-time incentive payments for signup based on percentage of rental rate and the practice,  $I_0(q)$ , and cost-share payment,  $CS_0(q)$ , as a share of cost to install a practice at time  $t=0$ .

Since payments to producers from conservation programs are public spending, the net present value of all economic costs,  $TC(q)$  also incorporate gains to producers expressed as:

$$TC(q) = \int_0^T [C_t(q) + R_t(q) + I_0(q)] e^{-rt} dt \quad (3)$$

where  $TC(q)$  represents all economic costs to be spent on establishing and maintaining a riparian buffer. Through cost-share payments the conservation program subsidizes the producers up to 87.5% of the initial cost to install the practice, so that the total cost  $TC(q)$  exclude cost-share payments from the total economic cost to avoid double counting.

To estimate the cost of reducing nutrients in waters using riparian buffers, the total economic costs needed to install the buffer are divided by the associated nitrogen (N) or phosphorus (P) reduction. If the annual reduction in nutrients (pollutants) is defined as  $P_i(q)$ , and the annual cost of reduction of nutrients is given as  $C(P_i)$ , then this annual cost per pollutant  $i$  can be expressed as:

$$C(P_i) = \frac{TC(q)}{T * P_i(q)} \quad (4)$$

We estimated the costs of reducing nutrients in the streams on a per acre basis by quantifying the amount of nutrients reduced per acre of buffer, based on the CBWM and our empirical data, and the annual economic cost of a buffer in present value on an acre of land.

#### ***4.5 Results***

Table 4.3 presents results of the economic assessment under CREP with net gains/loss to producers estimated over 15-year period in present value as of 2019. The estimates show the detailed costs and gains under each option to the producer or eligible CREP participants.

Key economic assumptions used in the analysis are detailed in Table 4.4. The assumptions include a discount rate of 5%; CREP contract term of 15 years; average soil rental rate for the cropland of each county obtained through the Allegany Soil Conservation District; establishment costs; and incentive payments under CREP. Analysis was also performed using 3% and 7% discount rates but was not included because the net gains were not substantially affected. Producer gains and costs were determined by placing economic values on the number of resources and services required for each practice's establishment. Note, the taxes from the payment are not accounted in this analysis. Additional background information on these options, along with the detailed estimates, are available upon request.

Through Maryland CREP the gains to the producers include:

- rental payments based on the soil rates in each county;
- cost-share payments under CREP as a percentage of the cost to install the practice;

- one-time incentive payments for land enrollment and installing practices; and
- the added incentive payments, as a percentage of the soil rental rate for installing the practice.

Table 4.3 Costs and benefits to producers establishing riparian buffers in Allegany and Washington Counties under CREP.

Benefits and Costs	Allegany			Washington		
	Grass Buffer	Forest Buffer	Forest Buffer & Natural Forest	Grass Buffer	Forest Buffer	Forest Buffer & Natural Forest
<i>Net Present Value in dollars per acre over a 15-year period</i>						
<i>Producer Gains:</i>						
Rental Payments	\$1,765	\$2,094	\$1,047	\$2,618	\$3,118	\$1,559
Incentive Payments: SIP, State Incentive Payment, and PIP	\$330	\$1,500	\$750	\$330	\$1,500	\$750
Cost Share Payments	\$284	\$2,844	\$1,422	\$284	\$2,844	\$1,422
<i>Producer Costs:</i>						
Establishment Cost	(\$325)	(\$3,250)	(\$1,625)	(\$325)	(\$3,250)	(\$1,625)
Mowing & Maintenance Cost	(\$378)	(\$503)	(\$251)	(\$378)	(\$503)	(\$251)
Foregone Income	(\$1,839)	(\$1,839)	(\$922)	(\$1,839)	(\$1,839)	(\$922)
<b>Net Gains (Loss)</b>	<b>(\$163)</b>	<b>\$846</b>	<b>\$421</b>	<b>\$690</b>	<b>\$1,870</b>	<b>\$933</b>

Notes: The table shows the gains and losses to the producers from the conversion of cropland to a riparian grass buffer, riparian forest buffer, and a riparian forest buffer next to a natural forest through the enrollment of Maryland's Conservation Reserve Enhancement Program (CREP). SIP is one-time signing incentive payment. PIP is one-time practice incentive payment. A cost share payment comprises of up to 50% of establishment cost to install the practice and 37.5% of the establishment cost from the State of Maryland. All estimates are calculated as of 2019. All future estimates discounted at 5%.

Table 4.4 Assumptions used in the economic analysis.

Assumptions	Grass Buffer	Forest Buffer	Forest Buffer & Natural Forest
Interest rate	5%	5%	5%
Years in program	15 years	15 years	15 years
Base soil rate in Allegany/Washington MD Counties	58/88	58/88	58/88
Incentive payment in % from the soil rate based on the practice per year	150%	200%	100%
One-time SIP and State payments	\$200	\$200	\$100
Establishment cost	\$350	\$3,250	\$1,625
One-time PIP (40% of establishment cost)	\$130	\$1,300	\$650
Cost-share payments (87.5% of establishment cost)	\$284	\$2,844	\$1,422
Maintenance payment for replanting <sup>1</sup>	\$96	\$91	\$45
Mowing cost per year <sup>2</sup>	\$40	\$40	\$40
Maintenance cost-share per year	\$10	\$10	\$5
Foregone income per year <sup>3</sup>	\$162	\$162	\$131

Note. <sup>1</sup>Maintenance for replanting a riparian forest buffer is considered for the 2nd year, and for the riparian grass buffer during the 4th & 8th years only. <sup>2</sup>Mowing cost with the riparian grass buffer is considered every other year. <sup>3</sup>Foregone income under the riparian forest buffer & natural forest includes an additional \$50 for timber harvests.

#### 4.5.1 Rental payments

These payments play a central part in setting the gains and costs for land enrollment and the practice installed under a long-term contract. Producer rental rates

vary by geographical location, with higher rents to be paid on more productive soils. Rental payments for the cropland in western Maryland are lower than the average producer rental rates in the state of Maryland. For simplicity, we consider that producers can earn \$58 and \$88 per acre in rental fees based on the correspondent average soil rental rates in Allegany and Washington Counties, plus the incentive bonus based on the conservation practice offered (150% or 200% of the rental rate for the riparian grass buffer or the riparian forest buffer). Combined rental rate and incentive payment for the practice represents the guaranteed annual rental payment to the producer of the cropland to be retired during the term of the contract. For the riparian buffer adjacent to a natural forest, the rent is considered only for the portion of the enrolled cropland.

Under CREP, the total rental payments are estimated in present value as of 2019 at \$1,765 per acre for a grass buffer without fencing, at \$2,094 per acre for a riparian forest buffer, and at \$1,047 for an enhanced (natural and planted) riparian buffer in Allegany County over 15 years. In Washington County, the total rental payments under three options are estimated at \$2,618, \$3,118, and \$1,559 (present value) per acre, respectively. Because of the differences in the soil rental rate and the practice, the rental payments vary significantly under the three options of cropland enrollment.

#### **4.5.2 Cost-share payments**

Cost-share payments are paid from federal and state funding to producers for establishing vegetative cover or implementing conservation practices under contracts. Cost-share payments are calculated based on the cost to install the practice. The enrolled producer receives a cost-share payment of up to 50% of their own cost to install a



practice from federal resources and 37.5% of the installation cost from the state (USDA and FSA 2018). The total cost-share payment was estimated at \$284 per acre for the grass buffer, \$2,844 per acre for the forest buffer, and \$1,422 per acre of the ½ natural and ½ newly planted forest buffer. A notable difference in the cost-sharing costs is because of higher installation cost to establish a riparian forest buffer compared to the cost for establishing a grass buffer.

#### **4.5.3 Incentive payments**

One-time incentive payments include a signing incentive payment (SIP) of \$100 per acre for establishing a grass buffer and \$150 per acre for installing a riparian buffer. The practice incentive payment (PIP) comprises of 40% from the cost for establishing the practice. In addition, the State of Maryland provides an incentive payment of \$100 per acre for land enrollment (USDA and FSA 2018). In sum, the total incentive payments under three scenarios range from \$330 to \$1,500 per acre in the first year of enrollment. The incentive payments are the highest for establishing a riparian forest buffer, which together with the cost-share payments amount to \$4,344 per acre, while it totals to \$614 per acre for the grass buffer. These numbers indicate that CREP provides substantial financial resources to the producers or landowners.

#### **4.5.4 Establishing and maintenance cost**

These costs represent the costs of voluntary practice installation and the maintenance cost. The direct costs to establish riparian forest buffers include seeds and tree costs, machinery and labor costs for planting, replanting, and maintenance. The costs also depend on the site location, types of trees planted, and tree shelters. In western

Maryland, tree shelters are necessary to protect trees from deer; therefore, they are included in the total cost for installing a forest buffer. Similar cost estimates for the forest buffer establishment have been reported in the range from \$218 to \$7,129 per acre to plant and maintain trees (Lynch and Tjaden 2000) and about \$2,657 per acre to establish and plant a buffer with shelters (Palone and Todd 1997). We used \$3,250 per acre as the cost to establish a riparian forest buffer with shelters, which was comparable to the 2019 average estimates of installing a forest buffer in Maryland and verified by USDA County Executive Director. In addition, we considered the cost on reinforcement plantings after 2 years from the buffer's establishment of about \$100 per acre and an annual mowing cost of \$40 per acre as of 2019. These costs are relevant to current expenditures of establishing forest buffers in western Maryland and to correspondent costs used by USDA in both counties.

For the grass buffer, the establishment costs also depend on the land location and the perimeter footage, vegetation to be planted, pesticide and herbicide, and labor and machinery costs to install the practice. The range of costs have been reported in the range from \$168 to \$400 per acre for the grass buffer (Lynch and Tjaden 2000), and from \$384 per acre for grass and legume strip to \$803 per acre for the hay filter strip (Nakao et al. 1999). We used the present cost of \$325 per acre for the filter strip establishment of the grass mixture and legumes per CREP recommended seed list, verified by USDA County Executive Director. In addition, we also included maintenance cost for reseeding the legume part of the grass mixture after the fourth year of \$96 per acre (twice per practice) and mowing cost of \$40 per acre every other year to control the vegetation growth.

Total present value of the maintenance and mowing costs for establishing the grass buffer was estimated at \$378 per acre. Establishing the riparian forest buffer was valued at \$503 per acre, and the adjacent forest buffer was estimated at \$251 per acre over 15 years. In some cases, the mixture of riparian buffer and the natural forest will require maintenance and the associated spending for the entire buffer. Because these types of operations are required, the additional costs on the natural forested buffer have been added in this analysis.

#### **4.5.5 Opportunity cost**

Cost of lost opportunity from establishing the riparian buffers represents the forgone income to the producers from their cropland taken out of production. To account for opportunity cost we consider a baseline scenario of corn production on no-till, non-irrigated cropland as estimated in the University of Maryland Extension “MD Crop Budgets” worksheet (Beale et al. 2017). With average yield of 150 bushels per acre and the 5-year average price of \$3.90 per bushel, the producer is assumed to gain net income of about \$162 per acre (net income over variable and fixed costs excluding the land charge). The gross revenue can vary depending on the crop production, its yield, and prices of the crop. The cost of inputs can also change depending on the soil, the input prices, and the production. In addition, the net income can be substantially lower since the cropland in riparian areas are typically less productive. For comparison, average forest and grass buffer opportunity costs across watersheds have been assumed at \$133 and \$119 per acre in 2010 dollars in the spreadsheet “Agricultural BMP Costs”. Note, according to the USDA Cash Rents Survey, the average annual rental rate in Maryland

for cropland is reported at \$109 per acre as of 2019. We consider the above baseline of the annual net income loss from the corn production valid, because only the cropland cost is treated as the fixed cost for the calculation of the forgone income for conservation practices (USDA NASS 2019). Under these assumptions, producers lose approximately \$1,839 per acre (present value) with riparian forest or grass buffers over 15 years.

#### **4.5.6 Net gains to producers**

Based on the per-acre net gain estimates, producers are expected to receive financial gains from the cropland enrollment with the riparian forest buffer and the unclassified forest buffer (enrollment of 0.5 acres) under CREP in both counties. The producers in Washington County also financially gain with establishment of the riparian grass buffer; however, the economic net gains are significantly lower than those for establishing a riparian forest buffer, but still greater than maintaining land in crop production. At the same time, producers in Allegany County are likely to receive the financial losses with the establishment of a streamside grass buffer. Such differences in net-benefits are attributed to the differences in soil quality, which determines the annual rental payments to producers over a 15-year period. Insufficient incentives and the projected financial losses to producers are known to contribute to declines in CREP enrollment in recent years.

#### **4.5.7 Economic costs of nutrient reduction**

Using equation 3 we estimated the present value of the economic costs of establishing a riparian buffer under three options over 15 years. These cost estimates are for the establishment and enhancement of a new buffer from the baseline year 2019

through 2034. Using equation 4, annual costs of nutrient reductions are calculated per kg of nitrogen and phosphorus for each buffer by dividing annual economic costs on a per acre basis by nutrient load reductions as described in Table 4.2 for each corresponding county.

Table 4.5 summarizes the present value of annual costs of nutrient reduction from establishing a buffer in each county as of 2019. Nutrient reduction costs vary based on the type of buffer in each region. The estimated costs of mitigating nitrogen range from \$5 per kg to \$53 per kg in Allegany County and from \$3 to \$59 per kg in Washington County. At the same time, phosphorus reduction costs are from \$18 to \$3135 per kg in Allegany County and from \$14 to \$8976 per kg in Washington County annually. The cost to reduce or prevent a kg of nitrogen from a forest buffer is about 50% higher than the corresponding average costs of nutrient reduction from the grass buffer in each county. For example, the mid-range costs to reduce nitrogen from grass buffers are \$13 and \$20 per kg in Allegany and Washington Counties, while the corresponding cost of nitrogen reduction from planted forest buffers are \$23 and \$30 per kg, respectively. At the same time, the mid-range costs per kg of phosphorus from grass buffers are higher than the comparable costs from forest buffers, such as \$1,585 vs \$1,446 per kg in Allegany County and \$4,502 vs \$1,618 per kg in Washington County, respectively. Conversely, the economic costs of phosphorus removal are likely to be higher for forest buffers than for grass buffers when the streamside buffer option is considered with exclusion fencing. These costs are not presented but available upon request. The differences in costs of nutrient removal vary across different buffer practices and indicate that certain buffers

could be more cost-effective for reducing nitrogen or phosphorus for a particular location.

Table 4.5 Economic costs of nutrient reductions in dollars per kg per year.

Nutrients/County	Grass Buffer*	Forest Buffer*	Forest Buffer - Narrow	Unclassified Forest Buffer*
<i>Allegany County, MD:</i>				
Nitrogen reduced, \$ per kg per year	\$5–\$20	\$11–\$35	\$38	\$5–\$53
Phosphorus reduced, \$ per kg per year	\$18–\$3135	\$38–\$2812	\$134	-
<i>Washington County, MD:</i>				
Nitrogen reduced, \$ per kg per year	\$3–37	\$5–54	\$19	\$6–\$59
Phosphorus reduced, \$ per kg per year	\$14–\$8976	\$25–\$3193	\$89	-

Notes: \*The lower bound estimate shows the cost of nutrient reduction based on the corresponding loads of nutrients for grass filter strip-streamside or forest buffer-streamside, while the upper bound shows the costs of a pollutant-based loads of nutrient reduction for grass or forest buffer.

\*\* The estimates show the mean costs of nitrogen reduction from natural and planted forest buffers based on the median loads determined by synoptic data in Chapters 2 and 3.

The median annual costs of nitrogen reductions in streams from the Unclassified Forest Buffer are estimated at \$5 and \$6 per kg in 2019 dollars in Allegany and Washington Counties. On a per site basis, these estimated costs range from \$5 to \$53 per kg of nitrogen in Allegany County and from \$6 to \$59 per kg in Washington County. The median annual cost is the same as the minimum economic cost even though the minimum

cost was calculated using the estimated nutrient reduction from the upper bound intercept. The calculations using the original intercept from the linear regression model and the upper bound intercept from the 95% prediction interval both generated a positive, non-zero TDN load in the 100% forested riparian area scenario. Therefore, when calculating the difference between the loads using the two scenarios (i.e., 100% and 0% buffered area) the differences remained the same even though the upper bound intercept predicted higher loads than the original intercept in both scenarios.

Comparing the median annual costs of the unclassified forest buffer to the mid-range costs of the grass and forest buffer indicates the unclassified forest buffer could be the most cost-effective practice for reducing nitrogen. This suggests that cost-effectiveness should be estimated for various types of riparian buffers established on the specific site with respect to specific pollutant reductions. In comparison, these methods can be more costly than others. The cost of removing one kg of N in a wastewater treatment facility ranges from \$7 to \$11 (Palone and Todd 1997) and P removal ranges from \$17 to \$46 (Keplinger et al. 2004). Structural and nonstructural best management practices implemented in urban and residential areas to control nutrients in stormwater runoff are estimated at \$20 per kg of N and \$78 per kg of P (EPA 2015).

The estimated costs are somewhat comparable to the annualized costs per kg of nutrients reduced per buffer that were estimated in 2018 dollars on the county level within CBWM and downloaded from the Chesapeake Assessment Scenario Tool (CAST). The utilized average cost of nitrogen removed are \$20 per kg with grass buffers and \$26 per kg with forest buffer in Allegany County and \$14 and \$19 per kg in Washington County, respectively. Somewhat lower average cost per kg of nitrogen is

reported for streamside grass and forest buffers with exclusion fencing at \$12 and \$14 in Allegany, and \$4 and \$5 per kg in Washington County, accordingly. With narrow grass and forest buffers, their average costs are at least twice more than the corresponding costs for the respective buffers. The highest costs of nitrogen removal are reported for the narrow grass and forest buffers with exclusion fencing where both costs were estimated at \$106 per kg in Allegany County, and \$37 and \$38 per kg in Washington County, respectively. The utilized average cost of phosphorus removal is higher for grass buffers than for forest buffers at \$2,811 per kg and \$1380 per kg in Allegany County and \$2536 and \$1610 per kg in Washington County, respectively. Note, that the annualized average costs per buffer used for estimation of cost per pollutant are incurred by public and provide entities, and therefore, not directly comparable to our total economic costs. But, even with such differences, the estimated values of nutrient mitigation indicate a notable variability in the costs based on which buffer to target, what location to plant the buffer, and which pollutant to mitigate.

In summary, the heterogeneity in economic costs is largely explained by the differences in the estimated loads of nutrients reduced by each buffer type. The hydrogeomorphology of the R&V also makes it necessary to predict how much nutrients are actually reduced per acre of planted buffer and naturally forested riparian area, since planted buffers may not reduce nutrients until they mature. In fact, our findings in Chapters 2 and 3 suggest insignificant correlations between planted buffers and nutrients in tested sites of western Maryland. While it is unclear if mature or younger vegetation is more efficient at abating nutrients, some studies show riparian buffers become more effective with age, requiring at least a decade of becoming established before seeing



water quality improvements (Peterjohn and Correll 1984, Lowrance et al. 1997, Addy et al. 1999, Mayer et al. 2007, Orzetti et al. 2010). Furthermore, in geographic regions with complex hydrologic flow regimes, signs of water quality improvement may take as long as 20 years depending on the groundwater residence time and the water source distribution of the stream (i.e., groundwater discharge, runoff, and springs) (Lindsey et al. 2003, Boyer 2005). The cost-effectiveness of a buffer for each nutrient is also contingent on economic cost of establishing the buffer and the regional characteristics. Ultimately, it is difficult to conclude the most-cost effective practice based on the estimated nutrient reductions using CBWM and our empirical model.

CBWM developed efficiencies based on averages calculated from an extensive literature review on buffer nutrient retention rates and collaborations between teams of professionals and scientists. Nonetheless they admit buffer efficiency is likely to be conditional and dependent on several factors that their model does not capture, such as hydrologic flow regimes that vary across hydrogeomorphic regions. They account for this variability by reducing the average BMP efficiencies that were found from the literature by 20%. Nonetheless, their model showed higher reduction rates than our linear regression model that uses synoptic data collected specifically from the R&V. Our model incorporated data collected during baseflow conditions, representing nutrient retention in subsurface flows only, and only assessed riparian forest buffers (not grass buffers). We also restricted the potential nutrient reductions by using 95% prediction intervals of the intercept and medians to define the range. This was in response to the data's highly skewed distribution that highlights the variability across these sites but made its minimum and maximum rates impractical to use in this study. Nonetheless, it

demonstrates the challenge of creating an accurate model within the R&V. Even the scientific community involved in creating the CBWM noted that we are in the rudimentary stage of modeling accurate nutrient efficiencies, especially across heterogenous landscapes.

#### **4.5.8 Environmental benefits**

Riparian buffers provide vital environmental benefits and ecosystem services. However, quantifying the monetary value of environmental benefits is challenging and beyond this paper. Had it been considered, the environmental benefits and ecosystem services from riparian buffers and improved water quality would have comprised the largest portion of the total economic benefits.

In particular, riparian forests are unique habitats that supports many components of biodiversity and ecosystem processes that can enhance habitat for birds, herpetofauna, and fish (Wainger and Mazzotta 2011). Riparian forests also provide habitat and protection to native aquatic and terrestrial organisms (Naiman et al. 2000, Richardson et al. 2005, Marczak et al. 2010) that enhance nutrient exchange between land and water (Nakano and Murakami 2001, Marczak and Richardson 2007). Riparian forests can also intercept sediment, provide shade, wood (carbon), and leaf-litter (nutrients) to streams that supports aquatic ecosystems and temperature sensitive species. Recreational fisheries contribute about \$500 million to Maryland's economy that relies on temperature sensitive species such as trout. Trees also reduce air pollution. A 20% reduction of air pollution could save farmers \$20 million from crop loss (Palone 1997).

Improved water quality of the Chesapeake Bay and its tributaries also supports various economic sectors and livelihoods. Annually, millions of kgs of seafood are harvested from the Bay and recreational opportunities, such as boating, fishing, and swimming, attract millions of tourists. Landowners and communities have also seen property values increase 20% by having cleaner waterways, recreational access, improved landscape aesthetics, flood protection, and erosion control. Retaining forests can reduce stormwater costs by \$57 million and prevent potential flooding where property damage can exceed \$250,000 per mile (Palone 1997). The Chesapeake Bay Foundation found that a healthy Bay and watershed provides economic benefits worth \$130 billion per year (McGee and Spencer 2014). The environmental benefits from improved water quality with riparian buffers in western Maryland are complex and require separate research investigation.

#### ***4.6 Discussion***

This study presents methods for estimating the economic costs and gains for establishing riparian buffers. A model for calculating the economic costs of reducing nutrients with riparian buffers has been introduced. The cost estimations for reducing nutrients in streams from riparian buffers was conducted in two counties comprised in the Ridge & Valley physiographic province in western Maryland. By incorporating the conditions of the Conservation Reserve Enhancement Program (CREP) for riparian buffers and the nutrient mitigation data, this analysis underlines the importance in considering the economic estimates and costs of nutrient reductions for different types of riparian buffers in different counties. While the positive net gains to producers can be

associated with riparian forest buffer restoration in general, the economic costs of nutrient reduction can vary across the watershed and riparian buffer practice.

When deciding which option to use, the producers should consider the soil quality of their property, the terms of the CREP contract, the opportunity cost, and the market conditions. Although riparian buffers are expected to bring economic gains to the producers under CREP, the cost to convert cropland to a riparian forest buffer is significantly larger than the cost of converting it to a grass buffer. At the same time, a riparian forest buffer costs at least twice more than the enhancement of buffers on a per-acre basis. The combination of a planted riparian buffer and a natural forest (unclassified forest buffer) was beneficial in improving water quality; yet its net gains to the producers are lower than the other practices. Producers do not receive economic payments for preserving natural riparian forests under the current conditions of CREP, nor can they receive substantial monetary incentives for enhancing a critical riparian area to extend a natural forest strip.

When extrapolating the agricultural buffer potential in Allegany and Washington Counties (Table 4.1), the total economic cost associated with enhanced riparian forest buffers are estimated to be \$0.6 and \$3.2 million (in 2019) in Allegany and Washington Counties, respectively, over the next 15 years. The total economic costs of newly planted riparian buffer restoration in two counties of western Maryland could reach around \$1.7 million and about \$8.7 million in present value in Allegany and Washington Counties over the next 15 years. The economic costs of establishing grass buffers would likely range from around \$0.8 million in Allegany County to about \$4.7 million (in 2019) in Washington County over the next 15 years. When considering potential nutrient

reductions, the unclassified forest buffer would reduce between 0.09 to 0.9 million kg of nitrogen across the two counties over a 15-year period. This assumes that sites defined as “agricultural buffer potential” are between naturally forested sites that would facilitate filling in buffer gaps. Otherwise, between 0.3 to 1.8 million kg of nitrogen is expected to be reduced from unconnected, individual 1-acre newly planted forest buffers and between 0.2 to 1.7 million kg from grass buffers. Phosphorus abatement from planted forest buffers is between 3,400 to 392,000 kg and grass buffers is between 1,360 and 389,000 kg per acre over 15 years.

Grass buffers could be the most cost-effective option to implement and mitigate more nutrients than both riparian forest buffer options. The forest and grass buffers’ estimated nitrogen reductions through the CBWM are almost equivalent, but the wide range of skewed results found using empirical data demonstrates the complexity of modeling nutrient reduction across the R&V, however, our study sites did not include grass buffers. The survival rate of trees planted through CREP are the lowest in the R&V compared to other provinces and may take more than 15 years to become functional. The slow establishment rate is a result of poor management, invasive species, and lack of local seed sources from native species that allow for natural regeneration (Bradburn et al. 2010). Grass buffers quickly form dense communities and survive year round which may be a better practice to implement within the R&V (Dosskey et al. 2010, Cole et al. 2020). The CBWM uses the most recent research to model nutrient retention efficacy of BMPs in different geographic areas (Chesapeake Bay Program 2019d), but more research is needed in the less studied physiographic provinces to confirm which buffer types are most effective and how much nutrients they will most likely retain. Even the most

complex models cannot capture the flowpath of subsurface waters that directly influence the filtering capacity of riparian buffers. Planting riparian forests near riparian areas already containing natural forests will facilitate the closure of buffer gaps, which would reduce the possibility of groundwater passing through an unbuffered area in karst terrain especially in the mountainous regions of western Maryland. Moreover, it would increase the likelihood that producers who established practices with forest cover would commit their land for a longer period due to lower productivity of the cropland in the region and higher costs to convert such land back into production. We acknowledge that this analysis is hypothetical. The planting of riparian buffers on properties already containing forest will not necessarily meet riparian buffer restoration goals, since naturally established forests do not count towards newly planted buffers under CREP. These buffers will, however, increase the area of continuously buffered streams and help to reach nutrient reduction goals.

#### ***4.7 Conclusion***

Our goal was to estimate the economic cost of nutrient reduction from riparian buffers and determine if they are worth implementing in the Ridge and Valley physiographic province in western Maryland through the Conservation Reserve Enhancement Program (CREP). We evaluated three scenarios: (1) converting cropland to a riparian grass buffer, (2) converting cropland to a riparian forest buffer, and (3) establishing riparian forest buffers next to a pre-existing natural forest along a stream. We found implementing a grass buffer is the most cost-efficient practice per kg of N/ P removed. However, the support and incentives provided to landowners for this

conservation practice are insufficient and landowners could potentially lose money. The most beneficial practice to the landowner is the installation of a 1-acre forest buffer, but installation costs are often very high. Although the landowner receives greater financial gains, nutrient reduction benefits are almost equivalent to the grass buffer.

We used the Chesapeake Bay Watershed Model (CBWM) and our own empirical data to estimate nutrient reduction loads. The CBWM rates were used for the first two scenarios and are higher than what our empirical results show. The CBWM includes surface and subsurface nutrient retention and ignores the heterogeneity of the R&V landscape. Our data was conducted at various sites throughout the R&V in western Maryland during baseflow conditions and focused on soluble forms of nutrients in subsurface waters. We found very few significant relationships between nutrients and newly planted riparian forest buffers, indicating forest buffers do not function to the level that CBWM suggests, but we cannot confirm the function of grass buffers. Our study sites containing planted and natural, mature forests showed more significant correlations with nutrients, implying that if the newly planted trees are managed properly, they will eventually become and perform like mature riparian forests. The amount of time needed for the trees to mature would most-likely require more than the 10- to 15- years allotted in the CREP contracts. Because it takes longer for riparian buffers to become functional in this region, it is important to preserve present riparian forests and assign longer contract periods. Our results showed the costs of mitigating nitrogen ranged from \$5.3 to \$54.0 per kg, which can be more costly than the removal of N in a wastewater treatment plant (i.e., \$11 per kg). Furthermore, this estimate may be severely underestimated if it takes years or decades before a riparian buffer becomes functional. Nonetheless, riparian

buffers provide multiple environmental benefits and ecosystem services whose values still make them worth implementing in regions such as the R&V. However, if nutrient reduction goals are the focus, then better land management and long-term riparian forest preservation is needed in tandem with other management practices.

#### ***4.8 Acknowledgements***

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## Chapter 5: Concluding remarks

This research provides insight into the hydrologic controls on stream water quality within the Ridge and Valley (R&V) physiographic province in western Maryland. Our findings indicate that stream-groundwater exchange and the predominant water sources (i.e., lateral groundwater, tributaries, and karst springs) significantly affect streamwater chemistry and the efficacy of riparian forest buffers. Our results were inconclusive in determining whether riparian forest buffers significantly reduce nutrient pollutants from reaching surface waters. However, our empirical evidence indicates that mature forested riparian areas more effectively reduce nutrient concentrations in streams than recently planted buffers, albeit we did not identify all of the mechanisms responsible for these nutrient reductions.

In Chapter 2, analyses using the two categories of ‘randomly selected’ and ‘special interest’ sites, which refers to sites containing recently planted buffers through CREP, found the ‘random’ sites had more significant negative correlations between nutrients and forested riparian areas than special interest sites (shown in Chapter 2, Table 2.1 A/B). When combining the recently planted with the random sites, more significant relationships were revealed, implying sites with recently planted buffers were functioning in some capacity but not at a significant level when analyzed alone. In Chapter 3, we again saw more significant relationships between nutrients and mature, forested riparian areas than recently planted buffers (Table 3.3B). We were then able estimate potential TDN reduction with percent forested riparian area by developing a simple linear regression model that combined sites from Chapters 2 and 3 that had natural and recently planted riparian buffers. Many outliers were removed before meeting all linear regression

model assumptions, but the relationship was significant each time the model was run. Phosphorus was never significantly correlated with percent forested riparian area when combining Chapters 2 and 3, even after several outliers were removed. The primary form of P in cropland runoff is usually in particulate form that is released during storm events. We sampled during baseflow and measured soluble forms of P, which may explain the lack of a significant relationship even though several significant relationships were found in both chapters.

Using a steady-state reach mass balance model to estimate the stream's contributing sources, we found several of our study reaches were either losing or largely gaining from tributaries and karst springs rather than groundwater. Gaining reaches from net lateral inflow, with minimal influence from tributaries and karst springs, were expected to show the most significant response to land use; however, we found no significant relationships in the subwatersheds demonstrating this characteristic. One watershed, Murleys Branch in Allegany County, showed the most significant response when only 16% and 35% of the mainstem was lateral groundwater, indicating that water source is not a strong predictor when identifying streams that will likely respond to land use. Furthermore, models predicted Washington County's discharge rate more accurately than Allegany County's, even though Washington County had more losing reaches than Allegany County. The presence of karst springs was not a significant factor in affecting predicted discharge rates. Karst-absent sites showed more variability and outliers between observed and predicted discharge rates than those with karst. However, we speculate that some of our results may be affected by mislabeling, as karst maps are

created based on karst potential and may lack the high-resolution capability needed to accurately assess our study reaches.

We conducted two synoptic stream chemistry studies across two counties in western Maryland to examine how groundwater, land use, and the presence of riparian forest buffers affect stream water quality. We used raw nutrient concentrations to estimate the change in nutrients from the upstream to downstream sites for gaining and losing reaches. By incorporating losing reaches, we expected no response to nutrient concentrations from land use. However, P declined with an increase in forest cover within the catchment and riparian area during one of the synoptic studies but showed a positive correlation with an increase in forested catchment in our second study. N also increased in response to planted riparian forest buffers.

Given the study range and sample size, we could not calculate the change in nutrient concentrations in lateral groundwater inflow for losing reaches; therefore, we analyzed gaining reaches only. Results exhibited several significant negative correlations between N and P species with forested catchment, forested riparian area (includes pre-existing, mature forest and newly planted buffers), and newly planted forest buffers only. Overall, nutrients showed the most consistent response to forested catchments. Some of the negative correlations found between nutrients and the forested riparian area had stronger negative correlations between nutrients and forested catchments, indicating stream water quality may depend more on upland land use. Nevertheless, forested riparian regions are considered more effective at reducing nutrients than recently planted buffers, according to results found in both synoptic studies. This indicates recently planted buffers have limited control on nutrient retention, but the combination of young

and mature forests can improve stream water quality. More time may also be needed for riparian forests to mature. The survival rate of planted trees through the Conservation Reserve Enhancement Program is lowest in the R&V compared to the other physiographic provinces within the Chesapeake Bay watershed. It may take more than 15 years (the maximum contract period in CREP) before the buffers become functional. Better land management, longer contract periods, and preservation of existing mature, riparian forests should be considered.

Isotope data showed evidence that most nitrate removals were from denitrification, which agrees with other studies that also concluded denitrification to be the primary mechanism in NO<sub>3</sub><sup>-</sup> removal (Addy et al. 1999, Parkyn 2004). Isotope data revealed correlations between denitrification and forested riparian area, even when nitrate concentrations exhibited no land cover response. Scatterplots also showed some mixing of tributaries and springs, which further supports the conclusion that stream water quality depends on its contributing water sources. Nonetheless, there is evidence that nutrients are being reduced through biological processes that could be in response to forested riparian regions.

ANC and ion data effectively showed how tributaries and karst springs influence the chemistry of the mainstem, which could also inhibit riparian forest buffers' effects in this region. Similarly, Gburek and Folmar (1999) found ionic concentrations (e.g., Ca, Mg, SO<sub>4</sub>, Cl, NO<sub>3</sub>, and HCO<sub>3</sub>) in streams depended on discharges from tributaries, where intensity depended on the land use from where they originated — higher concentrations were from heavily manured sites and low ionic concentrations were primarily from forests (Gburek and Folmar 1999b). Sporadically implementing riparian

forest buffers can reduce the overall nutrients in a stream but depending on the nutrient concentration and discharge rate of contributing waters, the mainstem's water quality may still be affected. Treating high nutrient levels in a tributary that significantly affects a mainstem's water quality may not be too onerous. However, a karst spring could be challenging, especially if the recharge location is unknown and there is limited space between the discharge location and stream channel. Furthermore, springs generally have higher flow rates and can discharge water thirteen times faster than diffuse flow, which could also affect mitigation strategies.

Riparian forest buffers may not have demonstrated strong effects on stream water quality in our study for several reasons. (1) The land use defined for these watersheds may be inaccurate due to catchment delineation tools following a landscape's topography. Subsurface hydrology in a karst landscape may follow a different flowpath than what the surface proposes; thus, some of the land uses we used to analyze each site's response may be inaccurate. (2) Newly planted riparian forests may need more time to mature. Root depth, density, biomass, and organic matter are expected to increase over time, creating more favorable conditions for denitrification and nutrient retention. (3) Deep aquitards could be impeding groundwater from filtering through the riparian region, where root depth from matured forests is more likely to intercept deeper groundwaters. (4) Locations where buffers were installed were exposed to higher percentage of agriculture within their catchments, which is what made them optimal sites to plant a riparian buffer. Therefore, they may be reducing the same amount of nutrients as mature forested riparian areas but the groundwater upland from the riparian area contains higher nutrient loads. (5) The residence time before seeing a response in water quality from implementing

riparian buffers may require several years. Models predicted streams in karst landscapes may begin showing a response to BMPs a decade after they are installed. This time frame depends on the water source distribution of the stream (i.e., groundwater discharge (young and old), runoff, and springs) (Lindsey et al. 2003). (6) Lastly, some of the stream reaches may have had other contributing sources that were missed during the synoptic survey and, therefore, not partitioned from the net lateral groundwater that could have affected our results.

Given the complex geology of the R&V, it is essential to understand if water quality prediction models work, primarily when they are used to estimate projected nutrient reductions from installing BMPs. We found models predicting water quality conditions using catchment-based land use and catchment area were inadequate, but a model using the actual measured discharge data was optimal. This demonstrates the hydrologic complexity that is insufficiently captured when only incorporating characteristics of the catchment. Many models ignore springs, seeps, and fractured conduits, which are essential to incorporate when applying models to the R&V. By incorporating the actual flow rate in our model, we can assume it captures some of these anomalies, thus making it a superior model for complex hydrological landscapes.

Chapter 4 focuses on the Conservation Reserve Enhancement Program (CREP) that was first established in Maryland in 1997 to restore the Chesapeake Bay's water quality. The program encourages landowners to install riparian buffers by offering monetary incentives and maintenance support to those who enroll in a 10- to 15-year contract period. We performed a benefit-cost analysis (BCA) to determine if the incentives adequately compensate landowners using three scenarios: (1) converting

cropland to a riparian grass buffer, (2) converting cropland to a riparian forest buffer, and (3) establishing riparian forest buffers next to a pre-existing natural forest along a stream.

Our BCA indicates that establishing a forest buffer is economically beneficial to the landowner, but those living in Allegany County may lose money if they install grass buffers. Higher incentives should be offered to promote plantings and encourage contract renewals, especially since it may take a decade after a BMP is installed for water quality to show signs of improving. BCA results were also used to estimate the economic cost of nitrogen and phosphorus reductions under the three scenarios. We used the Chesapeake Bay Watershed Model (CBWM) to estimate N and P reductions for newly planted forest buffers and grass buffers. We combined the sites from chapters 2 and 3 to estimate potential N reductions for the third scenario. Converting cropland to a grass buffer was the most cost-effective practice in reducing nutrients. Converting cropland to a riparian forest buffer was the most beneficial to landowners based on the economic gains. However, newly planted buffers did not appear to retain nutrients as effectively as the pre-existing, mature forests in our synoptic study. The CBWM uses efficiencies based on averages calculated from an extensive literature review, which does not capture the landscape's heterogeneity. Their model demonstrated higher reduction rates than what we estimated using our synoptic data. This lack of consensus in nutrient reductions again demonstrates how models may be inaccurate in evaluating riparian buffer function within the R&V.

This study could be improved by measuring in-stream nutrient processing that would strengthen the use of the steady-state reach mass balance model that was used to estimate net lateral groundwater inflow. We could also execute a more comprehensive

comparison between sites with planted and naturally forested riparian areas, including surveys of tree characteristics (e.g., growth, species, age, and density). Our methods also did not measure any of the riparian buffer mechanisms that can contribute to nutrient removal. Future studies should evaluate the hydrological flowpath, denitrification rates, and plant uptake. Also, evaluating riparian buffer function by measuring nutrient uptake rates within the riparian area, rather than nutrient changes within the stream may be more insightful. Furthermore, measuring the depth of the aquitard could give a better indication of subsurface flows through the riparian area, although many sites contained seeps that infer subsurface flows. Measuring the age of groundwater can give indication of the residence time of the flowpath and how long it may take for water quality to improve once a riparian buffer is installed.

Although we found some negative correlations between nutrient and land use, we did not see clear evidence supporting riparian forest buffers as an efficient mechanism in reducing nutrients from streams located throughout the R&V. This region presents challenges identifying the most useful sites to implement buffers due to flowpaths that bypass riparian zones and other characteristics that may be impacting buffer function. However, we suspect riparian buffers to be planted because of their importance as a BMP in other geographies. Our results show most nutrient reductions from forested riparian areas, including mature riparian forests and newly planted buffers. If the newly planted riparian forest buffers are adequately managed, they should eventually perform similarly to the mature forests. A stipulation of CREP is the contract period may be too short that does not allow enough time for forests to mature and effectively reduce nutrients. In the next few years, between 10 to 30% of buffers will expire under CREP. More extended

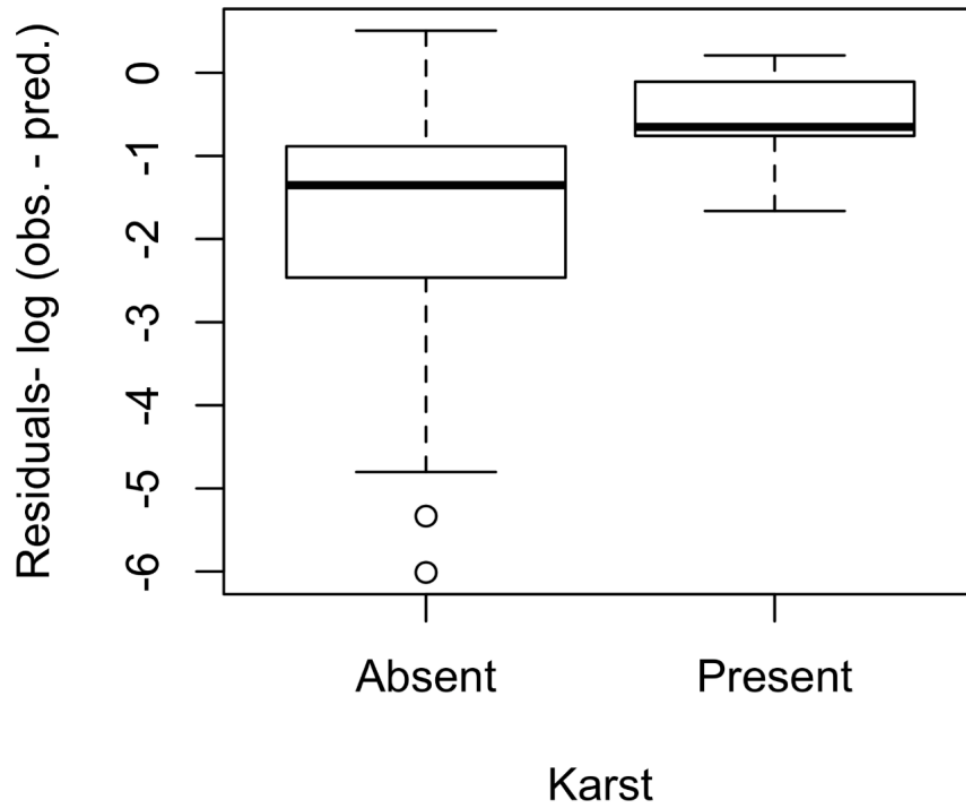


contract periods should be offered to give riparian buffers enough time to become established. Although riparian buffers may be implemented in locations where they may not be as efficient at retaining nutrients, they provide several vital environmental benefits and ecosystem services. They enhance habitats that promote biodiversity, protect native aquatic and terrestrial organisms, improve landscape aesthetics, and provide flood protection that should be considered as well.

## Appendices

### *Appendix A. Ch. 2 Boxplot, residuals between observed and predicted raw discharge data between karst and nonkarst sites.*

Boxplot showing visual between nonkarst (absent) and karst (present) sites and residuals of observed and predicted raw, log discharge data of WACO and ALCO sites only. Kruskal-Wallis found significance between the two groups (p-value 0.012).



*Note: two sites had to be removed (one ALCO (karst present) and one WACO (karst absent)) because their observed discharge was zero.*

**Appendix B. Ch. 3 Table of discharges of tributaries and karst springs**

Discharge of tributaries and karst springs of Murleys Branch (MB), Little Antietam Creek North (LACN), Beaver Creek (BC), and Little Antietam Creek South (LACS) normalized by their watershed area for all three sampling dates.

Sub-watershed	Site	Water Source	TCA (km <sup>2</sup> )	Q <sub>Norm</sub> (m/s)		
				SP16	FA16	SP17
MB	MB08	Tributary	0.28	0.00	NA	4.36E-09
MB	MB17	Tributary	1.75	1.60E-09	2.86E-10	9.26E-09
MB	MB19	Spring	0.68	6.14E-08	2.24E-08	1.55E-07
MB	MB24	Tributary	3.84	1.93E-09	2.35E-10	8.16E-09
MB	MB33	Tributary	0.46	2.19E-09	0.00	1.16E-08
MB	MB36	Tributary	0.31	3.59E-09	0.00	1.63E-08
MB	MB37	Tributary	3.84	1.17E-09	0.00	7.84E-09
MB	MB44	Tributary	6.87	3.13E-09	1.12E-09	1.15E-08
MB	MB50	Flintstone	0.09	2.51E-06	2.92E-07	1.35E-06
MB	MB52	Spring	0.19	1.32E-07	5.97E-08	3.54E-07
LACN	LAC108	Spring	0.97	4.58E-08	3.17E-08	3.71E-08
LACN	LAC120	Spring	6.49	5.60E-09	2.06E-09	1.14E-08
LACN	LAC125	Tributary	22.06	5.46E-09	1.92E-09	2.24E-08
LACN	LAC133	Tributary	13.05	3.70E-09	1.29E-09	2.99E-09
BC	BC03	Tributary	1.73	7.15E-09	1.21E-12	1.37E-08
BC	BC05	Tributary	0.69	3.28E-09	0.00	0.00
BC	BC19	Tributary	4.55	3.62E-09	0.00	1.75E-09
BC	BC29	Tributary	11.18	9.50E-09	1.48E-09	8.96E-09
BC	BC39	Spring	0.88	3.23E-07	1.53E-07	2.38E-07
BC	BC44	Tributary	11.18	8.48E-09	1.23E-09	9.22E-09
BC	BC68	Tributary	23.15	7.25E-09	5.90E-09	1.37E-08
LACS	LAC203	Tributary	1.72	4.32E-09	4.68E-10	1.05E-09
LACS	LAC210	Tributary	1.80	6.08E-09	9.25E-10	7.25E-09
LACS	LAC214	Tributary	4.86	1.77E-09	9.41E-12	5.76E-09
LACS	LAC228	Tributary	3.40	1.19E-09	0.00	7.82E-09
LACS	LAC233	Tributary	3.46	1.03E-10	0.00	2.98E-10
LACS	LAC245	Tributary	0.65	1.67E-10	0.00	0.00
LACS	LAC248	Tributary	17.81	5.58E-09	2.00E-09	1.09E-08
LACS	LAC254	Tributary	19.76	2.60E-09	5.85E-10	6.26E-09

Note: not all true watershed areas are known for karst springs.

**Appendix C. Ch. 3 MB results ( $\Delta C$ ) for Spearman's Rank Correlation test.**

Results of relationships between  $\Delta C$  (raw nutrients) versus % land cover. All reaches (losing & gaining) are included. Statistically significant values ( $P < 0.05$ ) are indicated in bold, blue font.

$\Delta$	Season	% Canopy		% FEHA		% Planted Buffer	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	0.61	0.13	0.18	0.34	0.96	-0.01
	Fall '16	0.38	-0.23	0.91	0.03	0.10	0.41
	Spring '17	0.89	0.04	0.18	0.34	0.61	0.13
<b>NH<sub>4</sub>-N</b>	Spring '16	0.90	-0.03	0.74	0.09	0.54	0.16
	Fall '16	0.72	-0.10	0.21	0.32	0.93	-0.02
	Spring '17	0.26	-0.29	0.70	0.10	0.23	0.31
<b>TDN</b>	Spring '16	0.55	0.15	0.13	0.38	0.96	-0.01
	Fall '16	0.37	-0.23	0.89	0.04	0.13	0.38
	Spring '17	0.69	-0.11	0.35	0.24	0.38	0.23
<b>PO<sub>4</sub>-P</b>	Spring '16	0.36	0.24	<b>0.04</b>	<b>0.50</b>	0.86	-0.05
	Fall '16	0.99	-4.9E-03	0.39	0.22	0.98	-0.01
	Spring '17	0.77	0.08	0.10	0.41	0.79	0.07
<b>TDP</b>	Spring '16	0.29	0.27	0.06	0.47	0.90	0.03
	Fall '16	0.92	0.03	0.22	0.32	0.90	-0.03
	Spring '17	0.53	0.16	0.21	0.32	0.61	-0.13
<b>TOC</b>	Spring '16	0.93	0.02	0.44	0.20	0.55	0.16
	Fall '16	0.44	-0.21	0.81	0.06	0.42	0.21
	Spring '17	0.24	-0.30	0.69	0.11	0.31	0.26
<b>Ca</b>	Spring '16	0.17	0.35	0.07	0.46	0.57	-0.15
	Fall '16	0.94	0.02	0.26	0.29	0.86	0.05
	Spring '17	0.74	-0.09	0.42	0.21	0.32	0.26
<b>Cl</b>	Spring '16	0.88	-0.04	0.61	0.13	0.87	-0.04
	Fall '16	0.16	-0.35	0.96	0.01	0.37	0.23
	Spring '17	0.51	-0.17	0.43	0.20	0.96	0.01
<b>Br</b>	Spring '16	0.88	-0.04	0.87	0.04	0.76	0.08
	Fall '16	0.43	-0.20	0.40	0.22	0.47	0.19
	Spring '17	0.64	-0.12	0.37	0.23	0.55	0.16
<b>K</b>	Spring '16	0.90	0.03	0.60	0.14	0.95	-0.01
	Fall '16	0.47	-0.19	0.50	0.18	0.45	0.20
	Spring '17	0.82	-0.06	0.24	0.30	0.94	0.02
<b>Mg</b>	Spring '16	0.79	0.07	0.36	0.24	0.90	-0.03
	Fall '16	0.24	-0.30	0.95	0.02	0.68	0.11
	Spring '17	0.99	-4.9E-03	0.26	0.29	0.95	0.02
<b>ANC</b>	Spring '16	0.24	0.30	0.09	0.42	0.97	0.01
	Fall '16	0.90	-0.03	0.34	0.25	0.50	0.17
	Spring '17	0.97	-0.01	0.29	0.27	0.36	0.24

**Appendix D. Ch. 3 MB results ( $C_{lat}$ ) for Spearman's Rank Correlation test.**

Results of relationships between  $C_{lat}$  (nutrients in lateral groundwater) versus % land cover. Only gaining reaches are included. Statistically significant values ( $P < 0.05$ ) are indicated in bold, blue font.

$C_{lat}$	Season	% Canopy		% FEHA		% Planted Buffer	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	0.87	0.06	0.96	-0.02	0.19	-0.41
	Fall '16	0.73	-0.12	0.56	0.20	0.09	-0.54
	Spring '17	0.10	-0.55	0.33	-0.35	0.76	0.11
<b>NH<sub>4</sub>-N</b>	Spring '16	0.42	-0.26	0.89	0.05	0.55	0.19
	Fall '16	0.15	0.46	0.80	0.09	0.48	-0.24
	Spring '17	0.49	-0.25	0.05	-0.64	0.46	0.27
<b>TDN</b>	Spring '16	0.85	0.06	0.65	-0.15	0.65	-0.15
	Fall '16	0.65	-0.15	0.56	0.20	0.10	-0.52
	Spring '17	<b>0.05</b>	<b>-0.65</b>	0.81	-0.09	0.79	0.10
<b>PO<sub>4</sub>-P</b>	Spring '16	0.35	-0.29	0.37	0.29	0.71	0.12
	Fall '16	0.60	0.18	0.50	0.23	0.21	-0.41
	Spring '17	0.81	0.09	0.84	-0.08	0.82	-0.08
<b>TDP</b>	Spring '16	0.14	0.45	0.29	0.34	0.66	0.14
	Fall '16	0.47	0.25	<b>0.05</b>	<b>0.62</b>	0.14	-0.48
	Spring '17	0.08	-0.59	0.10	-0.55	0.26	0.39
<b>TOC</b>	Spring '16	0.59	-0.17	0.38	-0.28	0.18	0.42
	Fall '16	0.40	-0.28	<b>0.03</b>	<b>-0.65</b>	0.29	0.35
	Spring '17	1.00	0.01	0.28	-0.38	0.55	0.21
<b>Ca</b>	Spring '16	0.64	-0.15	0.42	-0.26	0.36	-0.29
	Fall '16	0.37	-0.30	0.47	0.25	0.96	-0.02
	Spring '17	0.73	-0.13	0.28	0.38	0.55	-0.21
<b>Cl</b>	Spring '16	0.87	0.06	0.90	-0.04	0.28	0.34
	Fall '16	0.45	-0.25	0.49	-0.24	0.52	0.22
	Spring '17	0.54	0.22	0.13	0.52	<b>0.05</b>	<b>-0.63</b>
<b>Br</b>	Spring '16	0.35	-0.29	0.51	-0.21	0.28	0.34
	Fall '16	0.82	-0.08	0.16	0.45	0.45	0.26
	Spring '17	1.00	-0.01	0.92	-0.04	0.29	0.37
<b>K</b>	Spring '16	0.87	0.06	0.92	0.03	0.16	0.44
	Fall '16	0.16	-0.45	0.58	-0.19	0.25	0.38
	Spring '17	0.81	-0.09	0.28	-0.38	0.60	0.19
<b>Mg</b>	Spring '16	0.20	-0.40	0.30	-0.33	0.78	0.09
	Fall '16	<b>0.02</b>	<b>-0.69</b>	0.15	-0.46	0.46	-0.25
	Spring '17	0.17	-0.48	0.66	-0.16	0.74	0.12
<b>ANC</b>	Spring '16	0.43	-0.25	0.70	-0.13	0.24	-0.37
	Fall '16	0.45	-0.25	0.58	0.19	0.94	0.03
	Spring '17	0.28	-0.38	0.58	0.20	0.66	-0.16

**Appendix E. Ch. 3 LACN results ( $\Delta C$ ) for Spearman's Rank Correlation test.**

Results of relationships between  $\Delta C$  (raw nutrients) versus % land cover. All reaches (losing & gaining) are included. Statistically significant values ( $P < 0.05$ ) are indicated in bold, blue font.

$\Delta$	Season	% Canopy		% FEHA		% Planted Buffer	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	0.52	0.40	0.23	-0.70	1.00	0.00
	Fall '16	0.52	0.40	0.23	-0.70	1.00	0.00
	Spring '17	0.52	0.40	0.23	-0.70	1.00	0.00
<b>NH<sub>4</sub>-N</b>	Spring '16	0.68	0.30	0.95	0.10	0.45	0.50
	Fall '16	0.78	0.20	0.35	-0.60	0.95	0.10
	Spring '17	0.23	0.70	0.35	-0.60	0.52	0.40
<b>TDN</b>	Spring '16	0.52	0.40	0.23	-0.70	1.00	0.00
	Fall '16	0.52	0.40	0.23	-0.70	1.00	0.00
	Spring '17	0.52	0.40	0.23	-0.70	1.00	0.00
<b>PO<sub>4</sub>-P</b>	Spring '16	0.68	0.30	0.52	-0.40	0.95	-0.10
	Fall '16	0.52	0.40	0.23	-0.70	1.00	0.00
	Spring '17	0.95	0.10	0.68	-0.30	0.78	-0.20
<b>TDP</b>	Spring '16	0.95	0.10	0.68	-0.30	0.78	-0.20
	Fall '16	0.68	0.30	0.52	-0.40	0.95	-0.10
	Spring '17	0.95	0.10	0.68	-0.30	0.78	-0.20
<b>TOC</b>	Spring '16	0.78	0.20	0.35	-0.60	0.95	-0.10
	Fall '16	0.95	0.10	0.68	-0.30	0.78	-0.20
	Spring '17	0.35	-0.60	0.78	-0.20	0.23	-0.70
<b>Ca</b>	Spring '16	0.95	0.10	0.68	-0.30	0.78	-0.20
	Fall '16	0.95	0.10	0.68	-0.30	0.78	-0.20
	Spring '17	0.68	0.30	0.52	-0.40	0.95	-0.10
<b>Cl</b>	Spring '16	0.95	0.10	0.68	-0.30	0.78	-0.20
	Fall '16	0.68	0.30	0.52	-0.40	0.95	-0.10
	Spring '17	0.95	0.10	0.68	-0.30	0.78	-0.20
<b>Br</b>	Spring '16	0.78	0.20	0.35	-0.60	0.95	-0.10
	Fall '16	0.78	0.20	0.35	-0.60	0.95	-0.10
	Spring '17	0.68	0.30	0.95	0.10	0.95	0.10
<b>K</b>	Spring '16	0.78	0.20	0.35	-0.60	0.95	-0.10
	Fall '16	0.78	0.20	0.35	-0.60	0.95	-0.10
	Spring '17	0.78	0.20	0.35	-0.60	0.95	-0.10
<b>Mg</b>	Spring '16	0.95	0.10	0.68	-0.30	0.78	-0.20
	Fall '16	0.52	0.40	0.23	-0.70	1.00	0.00
	Spring '17	0.68	0.30	0.52	-0.40	0.95	-0.10
<b>ANC</b>	Spring '16	0.95	0.10	0.68	-0.30	0.78	-0.20
	Fall '16	0.95	0.10	0.68	-0.30	0.78	-0.20
	Spring '17	0.68	0.30	0.52	-0.40	0.95	-0.10

**Appendix F. Ch. 3 LACN results ( $C_{lat}$ ) for Spearman's Rank Correlation test.**

Results of relationships between  $C_{lat}$  (nutrients in lateral groundwater) versus % land cover. Only gaining reaches are included. Statistically significant values ( $P < 0.05$ ) are indicated in bold, blue font.

$C_{lat}$	Season	% Canopy		% FEHA		% Planted Buffer	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	0.78	-0.20	0.35	0.60	0.95	-0.10
	Fall '16	1.00	0.50	1.00	-0.50	1.00	0.50
	Spring '17	1.00	0.50	1.00	0.50	1.00	0.50
<b>NH<sub>4</sub>-N</b>	Spring '16	0.13	0.80	0.95	0.10	0.08	0.90
	Fall '16	1.00	0.50	1.00	-0.50	1.00	0.50
	Spring '17	0.33	1.00	1.00	-0.50	0.33	1.00
<b>TDN</b>	Spring '16	0.95	-0.10	0.68	0.30	0.78	-0.20
	Fall '16	1.00	0.50	1.00	-0.50	1.00	0.50
	Spring '17	1.00	0.50	1.00	0.50	1.00	0.50
<b>PO<sub>4</sub>-P</b>	Spring '16	0.68	-0.30	0.95	-0.10	0.45	-0.50
	Fall '16	1.00	0.50	1.00	-0.50	1.00	0.50
	Spring '17	1.00	0.50	1.00	0.50	1.00	0.50
<b>TDP</b>	Spring '16	0.95	0.10	0.68	-0.30	0.68	-0.30
	Fall '16	1.00	0.50	1.00	-0.50	1.00	0.50
	Spring '17	1.00	0.50	1.00	0.50	1.00	0.50
<b>TOC</b>	Spring '16	1.00	0.00	0.45	0.50	0.52	0.40
	Fall '16	1.00	-0.50	1.00	0.50	1.00	-0.50
	Spring '17	1.00	-0.50	1.00	-0.50	1.00	-0.50
<b>Ca</b>	Spring '16	0.78	0.20	0.08	0.90	0.45	0.50
	Fall '16	1.00	-0.50	1.00	0.50	1.00	-0.50
	Spring '17	1.00	0.50	1.00	0.50	1.00	0.50
<b>Cl</b>	Spring '16	0.52	-0.40	0.23	0.70	1.00	0.00
	Fall '16	1.00	0.50	1.00	-0.50	1.00	0.50
	Spring '17	1.00	-0.50	0.33	1.00	1.00	-0.50
<b>Br</b>	Spring '16	0.35	0.60	0.78	0.20	0.23	0.70
	Fall '16	1.00	0.50	1.00	-0.50	1.00	0.50
	Spring '17	1.00	-0.50	0.33	1.00	1.00	-0.50
<b>K</b>	Spring '16	0.52	0.40	0.68	0.30	0.23	0.70
	Fall '16	1.00	-0.50	1.00	0.50	1.00	-0.50
	Spring '17	1.00	0.50	1.00	0.50	1.00	0.50
<b>Mg</b>	Spring '16	0.78	-0.20	0.35	0.60	0.95	-0.10
	Fall '16	1.00	-0.50	1.00	0.50	1.00	-0.50
	Spring '17	1.00	0.50	1.00	0.50	1.00	0.50
<b>ANC</b>	Spring '16	0.78	0.20	0.08	0.90	0.45	0.50
	Fall '16	1.00	-0.50	1.00	0.50	1.00	-0.50
	Spring '17	1.00	0.50	1.00	0.50	1.00	0.50

**Appendix G. Ch. 3 BC results ( $\Delta C$ ) for Spearman's Rank Correlation test.**

Results of relationships between  $\Delta C$  (raw nutrients) versus % land cover. All reaches (losing & gaining) are included. Statistically significant values ( $P < 0.05$ ) are indicated in bold, blue font.

$\Delta$	Season	% Canopy		% FEHA		% Planted Buffer	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	1.00	0.00	0.64	-0.18	0.90	0.05
	Fall '16	0.78	0.20	0.95	0.10	0.87	-0.10
	Spring '17	0.61	-0.20	0.25	-0.43	0.95	-0.03
<b>NH<sub>4</sub>-N</b>	Spring '16	0.49	-0.27	0.21	-0.47	0.75	0.13
	Fall '16	0.23	-0.70	0.35	-0.60	0.22	-0.67
	Spring '17	0.70	-0.17	0.27	-0.45	0.80	-0.11
<b>TDN</b>	Spring '16	1.00	0.00	0.64	-0.18	0.90	0.05
	Fall '16	1.00	0.00	0.78	-0.20	0.74	-0.21
	Spring '17	0.75	0.14	0.62	-0.21	0.98	-0.01
<b>PO<sub>4</sub>-P</b>	Spring '16	0.27	-0.42	0.19	-0.48	0.47	-0.28
	Fall '16	0.35	-0.60	0.68	-0.30	0.74	-0.21
	Spring '17	0.43	-0.33	0.13	-0.60	0.93	-0.04
<b>TDP</b>	Spring '16	0.95	0.03	0.78	-0.12	0.40	-0.32
	Fall '16	0.23	-0.70	0.45	-0.50	0.93	0.05
	Spring '17	0.88	-0.07	0.30	-0.43	1.00	0.00
<b>TOC</b>	Spring '16	0.27	-0.42	0.18	-0.50	0.91	0.04
	Fall '16	0.23	-0.70	0.35	-0.60	0.22	-0.67
	Spring '17	0.84	-0.10	0.54	-0.26	0.26	-0.46
<b>Ca</b>	Spring '16	1.00	0.00	0.64	-0.18	0.90	0.05
	Fall '16	1.00	0.00	0.78	-0.20	0.74	-0.21
	Spring '17	0.93	-0.05	0.30	-0.43	0.65	0.19
<b>Cl</b>	Spring '16	0.81	-0.10	0.88	-0.07	0.86	-0.07
	Fall '16	0.95	0.10	0.78	0.20	0.55	-0.36
	Spring '17	0.39	-0.36	0.24	-0.48	0.93	-0.04
<b>Br</b>	Spring '16	0.44	-0.30	0.44	-0.30	0.68	-0.16
	Fall '16	0.95	-0.10	0.78	-0.20	0.93	0.05
	Spring '17	0.66	-0.19	0.24	-0.48	1.00	0.00
<b>K</b>	Spring '16	0.46	-0.28	0.34	-0.37	0.76	0.12
	Fall '16	1.00	0.00	0.78	-0.20	0.74	-0.21
	Spring '17	0.36	-0.38	0.15	-0.57	0.91	-0.05
<b>Mg</b>	Spring '16	0.84	0.08	0.95	-0.03	0.78	0.11
	Fall '16	0.78	0.20	0.95	0.10	0.87	-0.10
	Spring '17	0.75	-0.14	0.27	-0.45	0.67	0.18
<b>ANC</b>	Spring '16	0.91	0.05	0.78	-0.12	0.75	0.13
	Fall '16	0.78	0.20	0.95	0.10	0.87	-0.10
	Spring '17	1.00	0.00	0.79	-0.12	0.93	-0.04



**Appendix H. Ch. 3 BC results ( $C_{lat}$ ) for Spearman's Rank Correlation test.**

Results of relationships between  $C_{lat}$  (nutrients in lateral groundwater) versus % land cover. Only gaining reaches are included. Statistically significant values ( $P < 0.05$ ) are indicated in bold, blue font.

$C_{lat}$	Season	% Canopy		% FEHA		% Planted Buffer	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	1.00	-0.50	1.00	-0.50	1.00	0.50
	Fall '16	1.00	0.00	0.75	-0.40	0.26	0.74
	Spring '17	0.91	0.07	0.56	0.29	0.53	0.29
<b>NH<sub>4</sub>-N</b>	Spring '16	1.00	0.50	1.00	0.50	1.00	-0.50
	Fall '16	0.75	-0.40	0.92	-0.20	<b>0.05</b>	<b>-0.95</b>
	Spring '17	0.66	-0.21	0.35	-0.43	0.40	-0.38
<b>TDN</b>	Spring '16	1.00	-0.50	1.00	-0.50	1.00	0.50
	Fall '16	0.33	-0.80	0.08	-1.00	0.68	-0.32
	Spring '17	0.96	0.04	0.84	0.11	0.88	0.07
<b>PO<sub>4</sub>-P</b>	Spring '16	1.00	0.50	1.00	0.50	1.00	-0.50
	Fall '16	0.33	0.80	0.08	1.00	0.68	0.32
	Spring '17	0.17	-0.61	0.27	-0.50	0.91	0.05
<b>TDP</b>	Spring '16	0.33	1.00	0.33	1.00	1.00	0.50
	Fall '16	0.75	0.40	0.33	0.80	0.68	0.32
	Spring '17	0.14	-0.64	0.30	-0.46	0.91	0.05
<b>TOC</b>	Spring '16	1.00	0.50	1.00	0.50	1.00	-0.50
	Fall '16	0.33	-0.80	0.75	-0.40	<b>0.05</b>	<b>-0.95</b>
	Spring '17	0.30	-0.46	0.11	-0.68	0.43	-0.36
<b>Ca</b>	Spring '16	1.00	-0.50	1.00	-0.50	1.00	0.50
	Fall '16	1.00	0.00	0.75	-0.40	0.26	0.74
	Spring '17	0.91	-0.07	0.59	0.25	0.70	-0.18
<b>Cl</b>	Spring '16	1.00	-0.50	1.00	-0.50	1.00	0.50
	Fall '16	0.75	0.40	0.33	0.80	0.68	0.32
	Spring '17	0.35	-0.43	0.66	-0.21	0.16	-0.59
<b>Br</b>	Spring '16	1.00	-0.50	1.00	-0.50	1.00	0.50
	Fall '16	0.75	0.40	0.33	0.80	0.68	0.32
	Spring '17	0.27	-0.50	0.24	-0.54	0.21	-0.54
<b>K</b>	Spring '16	1.00	0.50	1.00	0.50	0.33	1.00
	Fall '16	0.75	0.40	0.33	0.80	0.68	0.32
	Spring '17	0.84	-0.11	0.78	0.14	0.88	-0.07
<b>Mg</b>	Spring '16	1.00	-0.50	1.00	-0.50	1.00	0.50
	Fall '16	0.33	0.80	0.75	0.40	<b>0.05</b>	<b>0.95</b>
	Spring '17	<b>0.03</b>	<b>-0.82</b>	0.27	-0.50	0.33	-0.43
<b>ANC</b>	Spring '16	1.00	-0.50	1.00	-0.50	1.00	0.50
	Fall '16	1.00	0.00	0.75	-0.40	0.26	0.74
	Spring '17	0.91	-0.07	0.59	0.25	0.70	-0.18

**Appendix I. Ch. 3 LACS results ( $\Delta C$ ) for Spearman's Rank Correlation test.**

Results of relationships between  $\Delta C$  (raw nutrients) versus % land cover. All reaches (losing & gaining) are included. Statistically significant values ( $P < 0.05$ ) are indicated in bold, blue font.

$\Delta$	Season	% Canopy		% FEHA		% Planted Buffer	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	0.40	0.39	0.40	0.39	0.35	0.43
	Fall '16	0.66	0.21	0.50	0.32	0.66	0.21
	Spring '17	0.35	0.43	0.66	0.21	0.50	0.32
<b>NH<sub>4</sub>-N</b>	Spring '16	1.00	0.00	0.20	0.57	0.50	0.32
	Fall '16	0.17	-0.61	0.56	-0.29	<b>0.05</b>	<b>0.79</b>
	Spring '17	0.50	-0.32	0.84	-0.11	0.14	0.64
<b>TDN</b>	Spring '16	0.40	0.39	0.40	0.39	0.35	0.43
	Fall '16	0.78	0.14	0.56	0.29	0.50	0.32
	Spring '17	0.35	0.43	0.66	0.21	0.50	0.32
<b>PO<sub>4</sub>-P</b>	Spring '16	0.27	-0.50	1.00	0.00	0.14	0.64
	Fall '16	0.27	0.50	0.59	0.25	0.17	0.61
	Spring '17	0.78	-0.14	0.09	-0.71	0.17	0.61
<b>TDP</b>	Spring '16	0.71	-0.18	0.66	0.21	0.17	0.61
	Fall '16	0.20	0.57	0.50	0.32	0.11	0.68
	Spring '17	0.91	0.07	0.27	-0.50	0.07	0.75
<b>TOC</b>	Spring '16	0.78	-0.14	0.11	0.68	0.84	0.11
	Fall '16	0.20	0.57	0.50	0.32	0.11	0.68
	Spring '17	0.66	0.21	0.20	0.57	0.50	0.32
<b>Ca</b>	Spring '16	0.91	-0.07	0.35	0.43	0.71	0.18
	Fall '16	0.44	0.36	0.35	0.43	0.96	0.04
	Spring '17	0.78	0.14	0.50	0.32	0.96	0.04
<b>Cl</b>	Spring '16	0.50	0.32	0.01	0.89	0.84	-0.11
	Fall '16	0.17	0.61	0.07	0.75	0.78	0.14
	Spring '17	0.30	0.46	0.11	0.68	0.84	0.11
<b>Br</b>	Spring '16	0.40	0.39	0.03	0.82	0.66	-0.21
	Fall '16	0.17	0.61	0.27	0.50	0.44	0.36
	Spring '17	0.14	0.64	0.14	0.64	0.50	0.32
<b>K</b>	Spring '16	0.91	-0.07	0.17	0.61	1.00	0.00
	Fall '16	0.44	0.36	0.44	-0.36	0.50	-0.32
	Spring '17	0.84	-0.11	0.56	0.29	0.24	0.54
<b>Mg</b>	Spring '16	0.78	-0.14	0.24	0.54	0.91	0.07
	Fall '16	<b>0.03</b>	<b>0.82</b>	0.07	0.75	0.91	0.07
	Spring '17	0.96	0.04	0.30	0.46	0.59	0.25
<b>ANC</b>	Spring '16	0.59	-0.25	0.59	0.25	0.56	0.29
	Fall '16	0.71	0.18	0.78	0.14	0.66	0.21
	Spring '17	0.84	0.11	0.40	0.39	0.78	0.14

**Appendix J. Ch. 3 LACS results ( $C_{lat}$ ) for Spearman's Rank Correlation test.**

Results of relationships between  $C_{lat}$  (nutrients in lateral groundwater) versus % land cover. Only gaining reaches are included. Statistically significant values ( $P < 0.05$ ) are indicated in bold, blue font.

$C_{lat}$	Season	% Canopy		% FEHA		% Planted Buffer	
		p-Value	$\rho$	p-Value	$\rho$	p-Value	$\rho$
<b>NO<sub>3</sub>-N</b>	Spring '16	0.24	-0.60	0.92	-0.09	0.14	-0.71
	Fall '16	0.17	-0.61	0.44	-0.36	0.14	-0.64
	Spring '17	0.80	-0.14	0.06	-0.83	0.36	-0.49
<b>NH<sub>4</sub>-N</b>	Spring '16	0.80	-0.14	0.50	-0.37	0.66	0.26
	Fall '16	0.09	-0.71	0.14	-0.64	0.96	-0.04
	Spring '17	0.56	0.31	0.42	-0.43	0.30	-0.54
<b>TDN</b>	Spring '16	0.18	-0.66	0.80	-0.14	0.18	-0.66
	Fall '16	0.09	-0.71	0.35	-0.43	0.27	-0.50
	Spring '17	0.80	-0.14	0.06	-0.83	0.36	-0.49
<b>PO<sub>4</sub>-P</b>	Spring '16	0.92	-0.09	0.50	0.37	0.92	-0.09
	Fall '16	0.20	-0.57	0.56	0.29	0.59	-0.25
	Spring '17	0.56	0.31	0.42	-0.43	0.30	-0.54
<b>TDP</b>	Spring '16	0.92	-0.09	0.24	0.60	0.80	-0.14
	Fall '16	0.20	-0.57	0.56	0.29	0.59	-0.25
	Spring '17	0.56	0.31	0.56	-0.31	0.66	0.26
<b>TOC</b>	Spring '16	0.80	0.14	0.80	-0.14	0.24	0.60
	Fall '16	0.09	-0.71	0.91	0.07	0.78	0.14
	Spring '17	0.92	0.09	0.10	0.77	0.30	0.54
<b>Ca</b>	Spring '16	0.06	-0.83	0.42	-0.43	0.66	-0.26
	Fall '16	0.44	-0.36	0.07	-0.75	0.56	-0.29
	Spring '17	0.66	-0.26	<b>0.02</b>	<b>-0.94</b>	0.80	-0.14
<b>Cl</b>	Spring '16	0.18	-0.66	0.80	-0.14	0.18	-0.66
	Fall '16	0.09	-0.71	0.84	-0.11	0.35	-0.43
	Spring '17	0.80	0.14	0.18	-0.66	0.24	-0.60
<b>Br</b>	Spring '16	0.18	-0.66	0.80	-0.14	0.18	-0.66
	Fall '16	0.14	-0.64	0.17	-0.61	0.78	-0.14
	Spring '17	0.50	0.37	0.50	0.37	0.71	-0.20
<b>K</b>	Spring '16	0.10	-0.77	0.50	-0.37	0.56	-0.31
	Fall '16	0.07	-0.75	0.09	-0.71	0.96	-0.04
	Spring '17	0.30	-0.54	0.02	-0.94	1.00	-0.03
<b>Mg</b>	Spring '16	0.06	-0.83	0.42	-0.43	0.66	-0.26
	Fall '16	0.24	-0.54	0.20	-0.57	0.50	-0.32
	Spring '17	0.10	-0.77	0.24	-0.60	0.50	-0.37
<b>ANC</b>	Spring '16	0.14	-0.71	0.24	-0.60	0.42	-0.43
	Fall '16	0.40	-0.39	<b>0.02</b>	<b>-0.86</b>	1.00	0.00
	Spring '17	0.36	-0.49	<b>0.03</b>	<b>-0.89</b>	0.92	-0.09

***Appendix K. Ch. 3 Significant correlations between LULC and  $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  for all subwatersheds.***

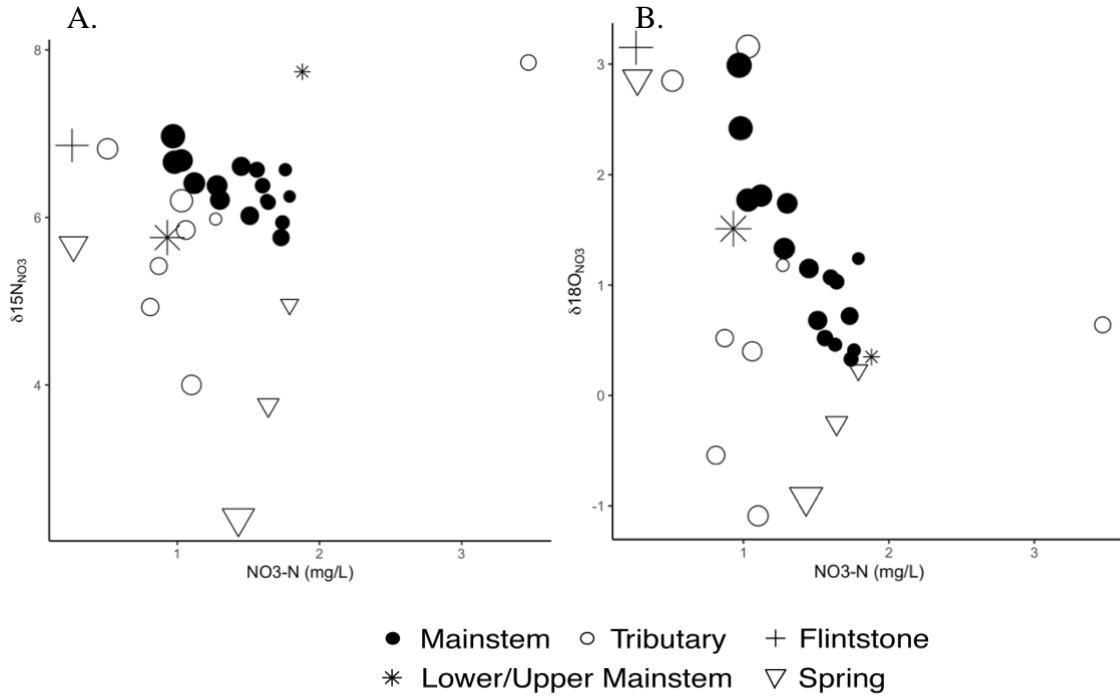
Nitrate isotopic data can indicate whether denitrification is occurring in response to particular land uses if there is a positive relationship with isotopic fractionation (i.e., increase in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$ ). When incorporating all our subwatersheds, we instead found negative relationships including:  $C_{\text{lat}} \delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  with percent canopy ( $\rho = -0.53$ ,  $P = 0.009$ ;  $\rho = -0.55$ ,  $P = 0.006$ , respectively) and  $C_{\text{lat}} \delta^{18}\text{O}$  and FEHA ( $\rho = -0.49$ ,  $P = 0.02$ ). Another signal of denitrification is a negative relationship between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  with  $\text{NO}_3\text{-N}$ ; but instead, positive relationships were exhibited between  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  and  $\text{NO}_3\text{-N}$  (raw ( $\rho = 0.38$ ,  $P < 0.001$ ) and  $\Delta$  ( $\rho = 0.71$ ,  $P < 0.001$ )) and  $\Delta\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  and  $\Delta\text{NO}_3\text{-N}$  ( $\rho = 0.39$ ,  $P = 0.02$ ).

***Appendix L. Ch. 3 Significant correlations between LULC and  $\delta^{15}\text{N}/\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  for individual subwatersheds.***

When analyzing subwatersheds separately, additional results were uncovered opposite from a denitrification signal. Negative correlations were found in MB between  $C_{lat}$  and  $\Delta\delta^{18}\text{O}$  with canopy ( $\rho = -0.65$ ,  $P = 0.05$ ;  $\rho = -0.70$ ,  $P = 0.002$ , respectively) and  $C_{lat} \delta^{18}\text{O}$  with FEHA ( $\rho = -0.64$ ,  $P = 0.05$ ). In MB, a positive relationship was also found between  $\Delta\delta^{15}\text{N}$  and  $\Delta\text{NO}_3\text{-N}$  ( $\rho = 0.82$ ,  $P < 0.001$ ). Other positive relationships were found in BC between raw  $\delta^{15}\text{N}$  and  $\text{NO}_3\text{-N}$  ( $\rho = 0.56$ ,  $P = 0.02$ );  $\Delta\delta^{15}\text{N}$  and  $\Delta\text{NO}_3\text{-N}$  ( $\rho = 0.72$ ,  $P = 0.04$ ); and  $\Delta\delta^{18}\text{O}$  and  $\Delta\text{NO}_3\text{-N}$  ( $\rho = 0.83$ ,  $P = 0.008$ ).

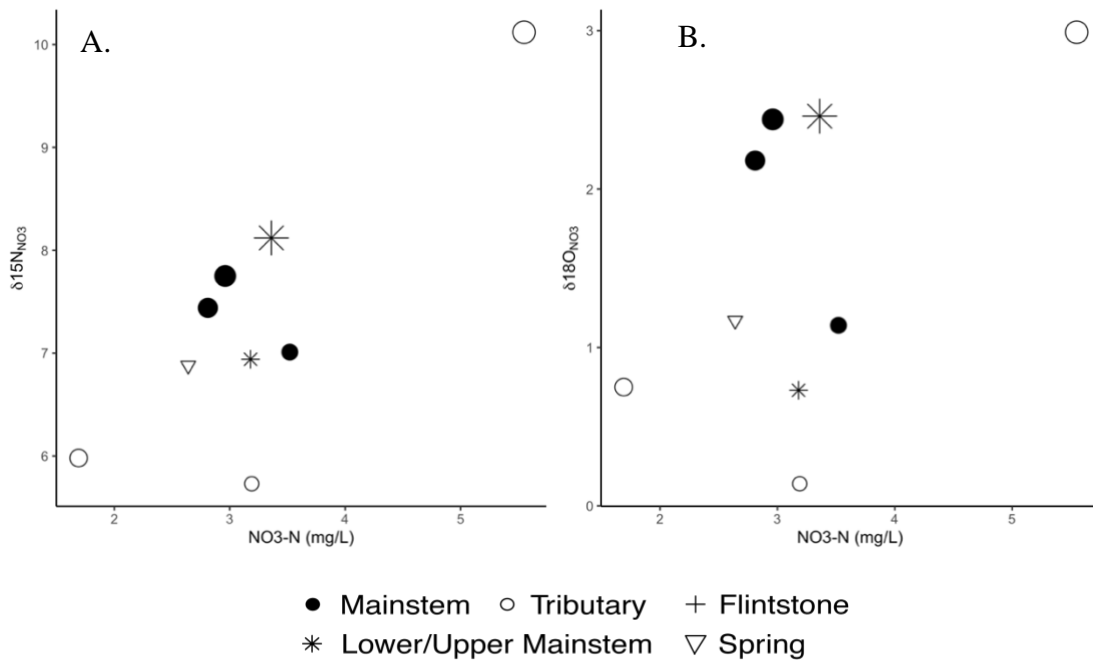
**Appendix M. Ch. 3 Murleys Branch isotope scatterplots.**

Fractionation of stable isotopes for Murleys Branch subwatershed of  $\text{NO}_3\text{-N}$  in surface water samples for  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  vs.  $\text{NO}_3\text{-N}$  (mg/L) (A) and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  vs.  $\text{NO}_3\text{-N}$  (mg/L) (B) for samples collected in spring 2017.



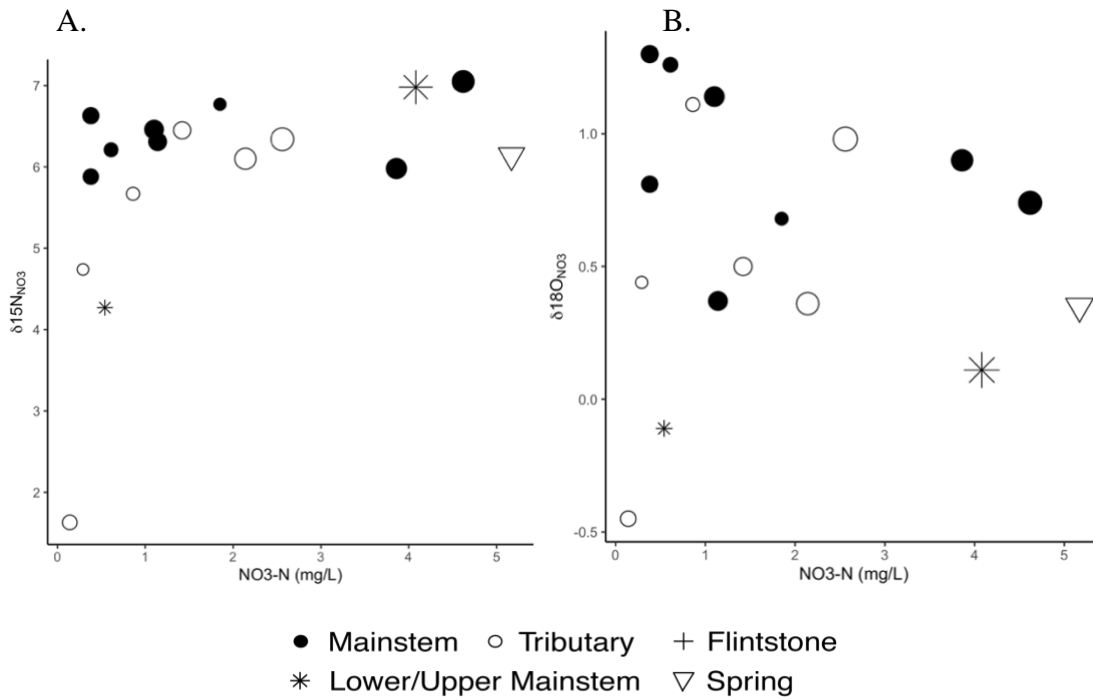
**Appendix N. Ch. 3 Little Antietam Creek North isotope scatterplots.**

Fractionation of stable isotopes for Little Antietam Creek North subwatershed of  $\text{NO}_3\text{-N}$  in surface water samples for  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  vs.  $\text{NO}_3\text{-N}$  (mg/L) (A) and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  vs.  $\text{NO}_3\text{-N}$  (mg/L) (B) for samples collected in spring 2016.



**Appendix O. Ch. 3 Beaver Creek isotope scatterplots.**

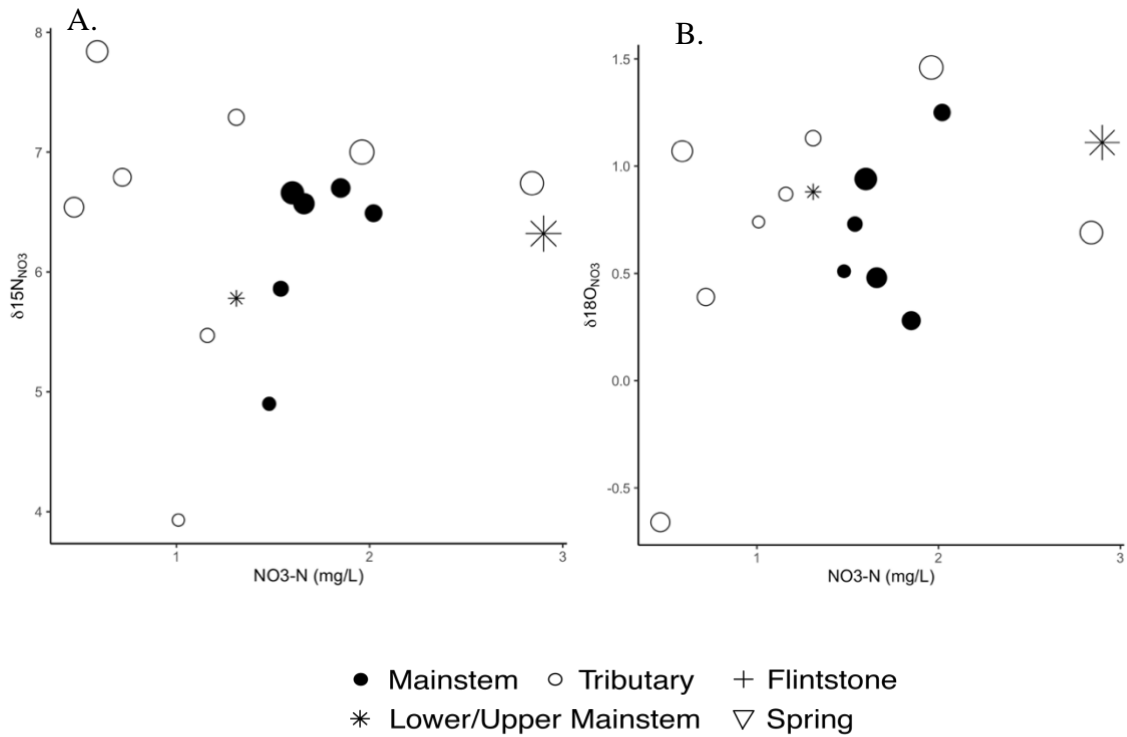
Fractionation of stable isotopes for Beaver Creek subwatershed of  $\text{NO}_3\text{-N}$  in surface water samples for  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  vs.  $\text{NO}_3\text{-N}$  (mg/L) (A) and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  vs.  $\text{NO}_3\text{-N}$  (mg/L) (B) for samples collected in spring 2016.





**Appendix P. Ch. 3 Little Antietam Creek South isotope scatterplots.**

Fractionation of stable isotopes for Little Antietam Creek South subwatershed of  $\text{NO}_3\text{-N}$  in surface water samples for  $\delta^{15}\text{N}_{\text{NO}_3\text{-N}}$  vs.  $\text{NO}_3\text{-N}$  (mg/L) (A) and  $\delta^{18}\text{O}_{\text{NO}_3\text{-N}}$  vs.  $\text{NO}_3\text{-N}$  (mg/L) (B) for samples collected in spring 2016.



*Appendix Q. Ch. 3 Murleys Branch model results.*

Murleys Branch results of Nash-Sutcliffe model efficiency coefficient (NSE), root mean square error (RMSE), and predicted constant concentration (Clat) for each constituent for the “base model” and “actual flows model”. Bolded results distinguish optimal model.

		Spring 2016		Fall 2016		Spring 2017	
		Base	Actual	Base	Actual	Base	Actual
NO <sub>3</sub> -N	E	0.80	<b>0.94</b>	<b>0.84</b>	0.67	0.68	<b>0.91</b>
	RMSE	0.14	<b>0.08</b>	<b>0.19</b>	0.27	0.16	<b>0.09</b>
	Clat	1.66	1.53	1.62	1.82	1.65	1.52
NH <sub>4</sub> -N	E	-0.02	<b>0.38</b>	<b>-0.65</b>	-0.82	<b>-0.06</b>	-0.29
	RMSE	3.00E-03	<b>2.00E-03</b>	3.00E-03	3.00E-03	3.00E-03	3.00E-03
	Clat	0.01	0.01	0.01	0.01	0.01	0.01
TDN	E	0.69	<b>0.91</b>	<b>0.87</b>	0.67	0.67	<b>0.87</b>
	RMSE	0.16	<b>0.09</b>	<b>0.17</b>	0.27	0.15	<b>0.10</b>
	Clat	1.78	1.65	1.67	1.88	1.69	1.65
PO <sub>4</sub> -P	E	<b>0.11</b>	0.07	-0.15	<b>0.39</b>	0.59	<b>0.78</b>
	RMSE	<b>7.00E-04</b>	8.00E-04	2.00E-03	<b>1.00E-03</b>	2.00E-03	<b>1.00E-03</b>
	Clat	0.00	0.00	0.01	0.01	0.00	0.00
TDP	E	0.54	<b>0.64</b>	-0.43	<b>0.19</b>	0.64	<b>0.77</b>
	RMSE	1.37E-03	<b>1.30E-03</b>	3.47E-03	<b>2.66E-03</b>	3.70E-03	<b>3.09E-03</b>
	Clat	0.00	0.00	0.01	0.01	0.00	0.01
TOC	E	0.56	<b>0.66</b>	-0.56	<b>-0.48</b>	0.33	<b>0.80</b>
	RMSE	0.14	<b>0.12</b>	0.38	<b>0.37</b>	0.16	<b>0.08</b>
	Clat	0.72	0.68	0.93	1.21	0.84	0.93
SO <sub>4</sub>	E	0.76	<b>0.91</b>	<b>0.98</b>	0.88	<b>0.96</b>	0.93
	RMSE	2.00	<b>1.22</b>	<b>1.10</b>	2.69	<b>0.56</b>	0.87
	Clat	18.85	18.20	20.35	16.81	16.72	17.89
Cl	E	0.86	<b>0.95</b>	0.85	<b>0.91</b>	0.32	<b>0.95</b>
	RMSE	0.68	<b>0.39</b>	1.35	<b>1.07</b>	1.13	<b>0.27</b>
	Clat	5.48	6.23	8.70	11.42	5.67	5.54
Br	E	<b>-0.16</b>	-0.40	<b>-0.22</b>	-0.44	-0.06	<b>0.11</b>
	RMSE	1.00E-03	1.00E-03	3.00E-03	3.00E-03	2.00E-03	2.00E-03
	Clat	0.01	0.01	0.01	0.01	0.01	0.01
Na	E	0.88	<b>0.96</b>	0.86	<b>0.92</b>	-0.31	<b>0.75</b>
	RMSE	0.28	<b>0.16</b>	0.73	<b>0.55</b>	0.72	<b>0.28</b>
	Clat	2.46	2.64	3.80	4.43	2.62	2.71
K	E	0.22	<b>0.65</b>	-0.49	<b>0.64</b>	0.66	<b>0.86</b>
	RMSE	0.16	<b>0.11</b>	0.22	<b>0.11</b>	0.13	<b>0.07</b>
	Clat	1.19	1.15	1.61	1.92	1.26	1.41
Mg	E	0.02	<b>0.96</b>	-0.04	<b>0.59</b>	0.67	<b>0.78</b>
	RMSE	2.54	<b>0.50</b>	2.07	<b>1.30</b>	0.99	<b>0.56</b>
	Clat	18.36	19.02	18.13	17.59	16.61	17.61
Ca	E	0.28	<b>0.85</b>	0.30	<b>0.66</b>	0.64	<b>0.86</b>
	RMSE	8.50	<b>3.82</b>	6.61	<b>4.61</b>	5.07	<b>3.24</b>
	Clat	78.50	72.43	77.58	84.04	81.92	80.99
Si	E	-	-	0.70	<b>0.78</b>	0.49	<b>0.85</b>
	RMSE	-	-	0.15	<b>0.13</b>	0.21	<b>0.11</b>
	Clat	-	-	3.75	3.81	3.15	2.99

*Appendix R. Ch. 3 Little Antietam Creek North model results.*

Little Antietam Creek North results of Nash-Sutcliffe model efficiency coefficient (NSE), root mean square error (RMSE), and predicted constant concentration (Clat) for each constituent for the “base model” and “actual flows model”. Bolded results distinguish optimal model.

		Spring 2016		Fall 2016		Spring 2017	
		Base	Actual	Base	Actual	Base	Actual
NO <sub>3</sub> -N	E	-8.49	<b>0.64</b>	-3.30	<b>0.56</b>	<b>0.72</b>	-0.04
	RMSE	0.80	<b>0.16</b>	0.69	<b>0.22</b>	<b>0.32</b>	0.62
	Clat	1.66	4.24	3.89	3.86	3.71	6.41
NH <sub>4</sub> -N	E	<b>0.37</b>	0.25	0.54	<b>0.60</b>	<b>0.56</b>	0.28
	RMSE	<b>0.01</b>	0.01	0.01	<b>0.01</b>	<b>0.01</b>	0.02
	Clat	0.05	0.02	0.04	0.00	0.07	0.09
TDN	E	0.44	<b>0.49</b>	-0.61	<b>0.40</b>	<b>0.71</b>	0.01
	RMSE	0.24	<b>0.22</b>	0.38	<b>0.22</b>	<b>0.38</b>	0.49
	Clat	4.11	4.58	3.89	4.25	4.21	7.14
PO <sub>4</sub> -P	E	-2.09	<b>0.60</b>	-2.52	<b>0.38</b>	-3.57	<b>0.70</b>
	RMSE	0.02	<b>0.01</b>	0.02	<b>0.01</b>	0.02	<b>0.01</b>
	Clat	0.03	0.02	0.04	0.03	0.03	0.05
TDP	E	-1.26	<b>0.68</b>	-2.11	<b>0.43</b>	-2.80	<b>0.66</b>
	RMSE	0.02	<b>0.01</b>	0.02	<b>0.01</b>	0.03	<b>0.01</b>
	Clat	0.04	0.03	0.05	0.05	0.05	0.06
TOC	E	0.67	<b>0.73</b>	<b>0.69</b>	0.53	<b>0.89</b>	0.83
	RMSE	0.11	<b>0.10</b>	<b>0.10</b>	0.12	<b>0.11</b>	0.13
	Clat	0.86	1.17	0.96	0.62	0.75	0.83
SO <sub>4</sub>	E	0.58	<b>0.72</b>	<b>0.91</b>	0.86	<b>0.53</b>	0.48
	RMSE	2.07	<b>1.57</b>	<b>1.61</b>	1.99	1.51	<b>1.34</b>
	Clat	13.33	17.12	11.94	14.51	13.13	25.17
Cl	E	<b>0.92</b>	0.81	<b>0.98</b>	0.91	<b>0.90</b>	0.79
	RMSE	<b>1.61</b>	2.49	<b>0.73</b>	1.63	<b>1.38</b>	2.03
	Clat	11.92	17.64	15.82	21.87	16.40	30.91
Br	E	<b>0.48</b>	-0.48	0.46	<b>0.69</b>	<b>-0.07</b>	-0.48
	RMSE	<b>1.00E-03</b>	2.00E-03	1.00E-03	<b>1.00E-03</b>	<b>1.00E-02</b>	1.00E-02
	Clat	0.02	0.02	0.02	0.02	0.02	0.02
Na	E	<b>0.95</b>	0.84	<b>0.94</b>	0.82	<b>0.86</b>	0.23
	RMSE	<b>0.88</b>	1.50	<b>0.85</b>	1.42	<b>1.46</b>	3.41
	Clat	5.41	8.51	8.62	10.53	13.20	21.03
K	E	<b>0.92</b>	0.68	<b>0.85</b>	0.70	<b>0.66</b>	0.59
	RMSE	<b>0.07</b>	0.15	<b>0.14</b>	0.20	<b>0.18</b>	0.20
	Clat	1.79	1.90	2.18	1.51	1.67	1.58
Mg	E	-1.11	<b>0.61</b>	<b>0.70</b>	0.66	<b>0.79</b>	-0.11
	RMSE	1.18	<b>0.51</b>	<b>1.02</b>	1.07	<b>1.28</b>	2.95
	Clat	20.79	21.64	21.17	19.97	20.43	31.70
Ca	E	0.42	<b>0.49</b>	<b>0.75</b>	0.64	<b>0.91</b>	0.11
	RMSE	3.67	<b>3.44</b>	<b>2.94</b>	3.53	<b>2.80</b>	9.01
	Clat	65.64	65.59	69.48	62.63	63.63	97.52
Si	E	-	-	-3.25	<b>-0.56</b>	<b>0.75</b>	0.66
	RMSE	-	-	0.31	<b>0.19</b>	<b>0.18</b>	0.21
	Clat	-	-	5.58	3.87	4.98	5.94

*Appendix S. Ch. 3 Beaver Creek model results.*

Beaver Creek results of Nash-Sutcliffe model efficiency coefficient (NSE), root mean square error (RMSE), and predicted constant concentration (Clat) for each constituent for the “base model” and “actual flows model”. Bolded results distinguish optimal model.

		Spring 2016		Fall 2016		Spring 2017	
		Base	Actual	Base	Actual	Base	Actual
NO <sub>3</sub> -N	NSE	0.51	<b>0.82</b>	0.62	<b>0.95</b>	0.57	<b>0.97</b>
	RMSE	1.13	<b>0.68</b>	1.27	<b>0.48</b>	0.73	<b>0.18</b>
	Clat	1.73	1.96	0.52	1.96	0.69	0.54
NH <sub>4</sub> -N	NSE	-0.22	<b>0.41</b>	<b>-0.10</b>	-0.68	-0.14	<b>0.47</b>
	RMSE	0.02	<b>0.02</b>	<b>0.03</b>	0.03	0.03	<b>0.02</b>
	Clat	0.01	0.00	0.00	0.00	0.00	0.01
TDN	NSE	0.50	<b>0.78</b>	0.63	<b>0.94</b>	0.53	<b>0.97</b>
	RMSE	1.18	<b>0.78</b>	1.39	<b>0.56</b>	0.85	<b>0.21</b>
	Clat	1.87	1.96	0.55	1.99	1.04	0.86
PO <sub>4</sub> -P	NSE	<b>0.13</b>	0.03	0.24	<b>0.47</b>	-0.12	<b>0.65</b>
	RMSE	<b>3.00E-03</b>	3.00E-03	0.01	<b>0.01</b>	0.01	<b>4.00E-03</b>
	Clat	0.01	0.01	0.00	0.03	0.01	0.01
TDP	NSE	<b>-0.15</b>	-0.34	0.28	<b>0.75</b>	-0.15	<b>0.48</b>
	RMSE	0.01	<b>0.00</b>	0.01	<b>0.01</b>	0.01	<b>0.01</b>
	Clat	0.02	0.01	0.00	0.04	0.00	0.01
TOC	NSE	<b>-0.31</b>	-0.41	0.22	<b>0.81</b>	-1.04	<b>0.88</b>
	RMSE	<b>0.57</b>	0.59	0.60	<b>0.29</b>	0.89	<b>0.21</b>
	Clat	1.30	0.35	0.00	0.51	2.21	1.96
SO <sub>4</sub>	NSE	0.48	<b>0.86</b>	0.39	<b>0.60</b>	0.16	<b>0.93</b>
	RMSE	5.22	<b>2.75</b>	13.08	<b>10.64</b>	5.95	<b>1.72</b>
	Clat	10.26	7.94	4.66	23.45	13.23	9.49
Cl	NSE	0.51	<b>0.75</b>	0.29	<b>0.93</b>	0.05	<b>0.97</b>
	RMSE	6.95	<b>4.96</b>	12.46	<b>3.88</b>	11.19	<b>1.95</b>
	Clat	39.76	32.09	0.00	13.94	32.01	29.60
Br	NSE	<b>0.48</b>	0.10	0.60	<b>0.97</b>	-0.01	<b>0.89</b>
	RMSE	<b>4.00E-03</b>	5.00E-03	7.00E-03	<b>2.00E-03</b>	6.00E-03	<b>2.00E-03</b>
	Clat	0.01	0.02	0.00	0.01	0.01	0.01
Na	NSE	0.44	<b>0.84</b>	0.34	<b>0.89</b>	0.03	<b>0.98</b>
	RMSE	2.80	<b>1.50</b>	7.25	<b>2.98</b>	8.02	<b>1.21</b>
	Clat	16.37	11.63	0.00	7.99	23.49	20.12
K	NSE	0.43	<b>0.48</b>	0.75	<b>0.95</b>	0.28	<b>0.96</b>
	RMSE	0.29	<b>0.28</b>	0.70	<b>0.32</b>	0.56	<b>0.13</b>
	Clat	2.17	1.92	0.00	2.38	1.42	1.28
Mg	NSE	0.52	<b>0.52</b>	0.90	<b>0.97</b>	0.60	<b>0.98</b>
	RMSE	4.84	<b>4.79</b>	4.77	<b>2.17</b>	3.80	<b>0.88</b>
	Clat	12.06	13.63	1.06	19.34	6.58	4.38
Ca	NSE	0.51	<b>0.53</b>	0.82	<b>0.98</b>	0.58	<b>0.97</b>
	RMSE	15.11	<b>14.71</b>	15.10	<b>4.82</b>	11.42	<b>2.88</b>
	Clat	36.95	40.15	6.82	62.28	19.37	12.64
Si	NSE	-	-	0.00	<b>0.97</b>	-0.44	<b>0.90</b>
	RMSE	-	-	2.20	<b>0.40</b>	1.79	<b>0.23</b>
	Clat	-	-	4.85	4.70	4.36	4.90

*Appendix T. Ch. 3 Little Antietam Creek South model results.*

Little Antietam Creek South results of Nash-Sutcliffe model efficiency coefficient (NSE), root mean square error (RMSE), and predicted constant concentration (Clat) for each constituent for the “base model” and “actual flows model”. Bolded results distinguish optimal model.

		Spring 2016		Fall 2016		Spring 2017	
		Base	Actual	Base	Actual	Base	Actual
NO <sub>3</sub> -N	NSE	<b>0.43</b>	0.34	<b>0.48</b>	0.44	<b>0.90</b>	0.72
	RMSE	<b>0.35</b>	0.37	<b>0.42</b>	0.43	<b>0.11</b>	0.19
	Clat	2.52	2.20	3.56	2.54	3.73	2.80
NH <sub>4</sub> -N	NSE	-0.33	<b>-0.32</b>	<b>-0.43</b>	-0.61	0.02	<b>0.17</b>
	RMSE	3.40E-03	<b>3.30E-03</b>	<b>7.90E-03</b>	8.00E-03	1.70E-03	<b>1.60E-03</b>
	Clat	0.01	0.01	0.01	0.01	0.01	0.01
TDN	NSE	<b>0.45</b>	0.34	<b>0.38</b>	0.34	<b>0.87</b>	0.70
	RMSE	<b>0.33</b>	0.36	<b>0.47</b>	0.49	<b>0.13</b>	0.20
	Clat	2.57	2.29	3.68	2.68	3.92	3.02
PO <sub>4</sub> -P	NSE	0.22	<b>0.69</b>	0.82	<b>0.59</b>	0.63	<b>0.66</b>
	RMSE	5.00E-03	<b>3.00E-03</b>	<b>3.00E-03</b>	5.00E-03	4.00E-03	<b>4.00E-03</b>
	Clat	0.00	0.01	0.01	0.02	0.00	0.02
TDP	NSE	0.74	<b>0.78</b>	<b>0.83</b>	0.57	<b>0.69</b>	0.53
	RMSE	3.30E-03	<b>3.02E-03</b>	<b>2.90E-03</b>	4.56E-03	<b>3.50E-03</b>	4.35E-03
	Clat	0.00	0.01	0.02	0.02	0.00	0.02
TOC	NSE	-0.53	<b>-0.32</b>	0.67	<b>0.13</b>	<b>0.36</b>	0.74
	RMSE	0.17	<b>0.16</b>	<b>0.15</b>	0.25	0.10	<b>0.06</b>
	Clat	1.11	1.23	0.77	1.19	1.04	1.16
SO <sub>4</sub>	NSE	<b>0.66</b>	0.45	<b>0.70</b>	0.36	<b>0.55</b>	0.15
	RMSE	<b>1.26</b>	1.61	<b>1.39</b>	2.04	<b>0.77</b>	1.22
	Clat	11.51	10.13	14.22	11.79	14.61	10.70
Cl	NSE	<b>0.87</b>	0.46	<b>0.70</b>	0.31	<b>0.84</b>	0.49
	RMSE	<b>1.32</b>	2.72	<b>2.38</b>	3.64	<b>1.54</b>	2.74
	Clat	23.00	19.35	27.63	22.83	32.70	22.39
Br	NSE	-0.24	<b>-0.20</b>	-0.24	<b>-0.13</b>	<b>0.32</b>	0.13
	RMSE	3.00E-03	<b>3.00E-03</b>	2.00E-03	<b>2.00E-03</b>	<b>1.00E-03</b>	1.00E-03
	Clat	0.02	0.01	0.02	0.02	0.02	0.02
Na	NSE	<b>0.83</b>	0.44	<b>0.96</b>	0.49	<b>0.67</b>	0.48
	RMSE	<b>1.20</b>	2.18	<b>0.54</b>	1.96	<b>2.48</b>	3.13
	Clat	8.95	8.70	10.31	10.47	12.88	9.39
K	NSE	<b>0.62</b>	0.44	<b>0.57</b>	0.25	<b>0.61</b>	0.59
	RMSE	<b>0.26</b>	0.31	<b>0.34</b>	0.45	<b>0.27</b>	0.28
	Clat	1.21	1.52	1.55	2.09	1.08	1.07
Mg	NSE	<b>0.62</b>	0.50	<b>0.56</b>	0.34	<b>0.49</b>	0.30
	RMSE	<b>2.11</b>	2.41	<b>2.76</b>	3.38	<b>1.45</b>	1.70
	Clat	9.67	9.11	12.57	11.77	10.20	7.19
Ca	NSE	<b>0.51</b>	0.42	<b>0.44</b>	0.32	<b>0.34</b>	0.14
	RMSE	<b>11.42</b>	12.44	<b>14.61</b>	16.14	<b>7.22</b>	8.28
	Clat	41.79	38.84	56.96	50.37	39.79	27.12
Si	NSE	-	-	<b>0.89</b>	0.50	<b>0.85</b>	0.76
	RMSE	-	-	<b>0.56</b>	1.21	<b>0.69</b>	0.89
	Clat	-	-	8.61	7.21	8.64	8.38

### ***Appendix U. Ch. 3 Best model for each constituent.***

Appendices Q–T presents the values, along with the predicted constant mean ( $C_{lat}$ ) concentrations of all constituents for MB, LACN, BC, and LACS watersheds, respectively. The more superior model is indicated by the bold font (i.e., NSE values closer to 1 and RMSE values closer to 0). Because NSE is sensitive to bias, a model was reported as optimal only when NSE and RMSE values were in accordance, depending on their respected criteria (Ritter and Muñoz-Carpena 2013) (Ritter and Muñoz-Carpena 2013).

Investigation of individual subwatersheds found that in MB, LACN, and BC, the “actual flow model” was optimal for  $\text{NO}_3\text{-N}$ , TDN,  $\text{PO}_4\text{-P}$ , and TDP for at least two out of the three sampling dates. For LACS, the “base model” was the superior, showing a better predictor for  $\text{NO}_3\text{-N}$ , TDN, TDP, as well as majority of the less biologically reactive constituents (i.e.,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{SiO}_2$ ) for all three sampling dates, except for TDP in spring 2016. LACN also found the “base model” to be the better predictor for the less biologically reactive constituents, but MB and BC found the “actual flow model” to be optimal. For all four subwatersheds,  $\text{NH}_4\text{-N}$  did not follow the same trends as the other N species ( $\text{NO}_3\text{-N}$  and TDN) because of the low values, resulting in a low predicted  $C_{lat}$  that made it challenging to model accurately.

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