

**STREAM BANK LEGACY SEDIMENT CONTRIBUTIONS  
TO SUSPENDED SEDIMENT AND NUTRIENT EXPORTS FROM A  
MID-ATLANTIC, PIEDMONT WATERSHED**

by

Grant Jiang

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## **ABSTRACT**

While stream bank erosion has been increasingly recognized as a major source of fine sediment to watersheds, little research has been done on stream bank nutrient concentrations and their potential contributions to watershed nutrient budgets. This uncertainty is exacerbated by the ubiquitous presence of legacy-sediment impacted stream banks in the Mid-Atlantic region of the United States. This study applies the established sediment fingerprinting technique to quantify sediment source contributions to storm suspended and stream bed sediments in the Big Elk Creek, an agricultural Mid-Atlantic tributary of the Chesapeake Bay. Source sediments were collected from agricultural, developed, and forested soils as well as stream banks within the watershed, and ten storms were sampled at three locations within the watershed over the study period of August 1, 2017 to July 31, 2018. Stream bed samples were also collected once a month from each of the three field sites, to investigate if and how stream bed sediments interact with storm-mobilized sediments. We then applied the sediment fingerprinting technique to apportion sediment-bound nutrient yields into their constituent sources using Sed\_SAT, a sediment fingerprinting toolbox developed by and available through the United States Geological Survey.

Our key findings are first: stream bank sediments constitute a significant source of sediment to storm suspended and stream bed sediments; second: although stream bank contributions are generally higher during the Winter and Spring months, source sediment contributions are largely uncoupled from streamflow conditions; and third: we find that stream bank erosion accounts for 44% of watershed sediment yields by percent contribution, and 50% of sediment yields by mass. We further find that

stream banks have significantly lower nutrient (carbon, nitrogen, and phosphorus) concentrations than the sampled upland sediments, and thus only contribute 32% of sediment-bound carbon, 26% of sediment-bound nitrogen, and 32% of sediment-bound phosphorus to watershed nutrient yields. Our findings of 50% stream bank contribution to sediment yields and 32% contribution to phosphorus yields are comparable to Phase 6 Chesapeake Bay Model results for the Big Elk Creek.

This thesis expands upon our current understanding by quantifying stream bank contributions to watershed sediment and nutrient yields. In-channel pollutant generation from stream banks and beds is currently neglected or overlooked in most watershed management and restoration practices. The results of this thesis indicate that stream bank sediments and nutrients must be accounted for in watershed models, best management practices, and total maximum daily loads to ensure that pollutant mitigation and watershed restoration efforts are not mistargeted.

## Chapter 1

### INTRODUCTION

Sediments and sediment-bound contaminants have been identified as the leading cause of water quality impairment in the nation's water bodies (USEPA, 2016). Fifty-three percent of the nation's rivers and streams and 80% of the bays and estuaries assessed by the EPA have been classified as threatened or impaired (USEPA, 2016). Fine sediment can reduce light penetration thus reducing photosynthesis and primary productivity in water bodies (Van Nieuwenhuysse and LaPerriere, 1986); reduces the organic content of periphyton cells (Cline et al., 1982), damages macrophyte leaves and stems due to abrasion (Lewis, 1973), prevents algal cells from attaching to the substrate, and smothers periphyton aquatic macrophytes under extreme circumstances (Brookes, 1986). In addition, silt and clay-sized sediments are ideal vectors for other aquatic pollutants, such as phosphorus, nitrogen, heavy metals, and other contaminants deleterious to human and aquatic health (Waters, 1995; Wood and Armitage, 1997; Gellis et al., 2016; Henley et al., 2000). The Chesapeake Bay, the largest estuary in North America and a vital economic and ecological resource, has been classified as an impaired body of water since 2000 (Langland et al., 2003). An estimated  $7.3 \times 10^6$  Mg yr<sup>-1</sup> of suspended sediment is generated within the Chesapeake Bay watershed annually, of which 51% is attributed to agricultural lands, 31% from developed lands, 8% from small stream channels, and 2% from forested areas (Brakebill et al., 2010). More than \$3.6 Billion is being invested (over 2011-2025) in

agricultural best management practices (BMPs) for mitigating sediment and nutrient pollution from these various sources (Kaufman et al., 2014).

While contemporary upland sources are recognized as important sources of nonpoint source (NPS) pollution, there is an increasing realization that historic/legacy sediments stored in valley-bottoms and along streambanks could also be significant contributors of sediments and nutrients (Kleinman et al., 2011; Sharpley et al., 2013; Walter and Merritts, 2008; Miller et al., 2019). Legacy sediment sources are particularly notable in the northeast and the Mid-Atlantic region of the US where historic (and contemporary) land use practices associated with agricultural erosion and colonial era milldams (many of which have breached) have resulted in large valley bottom deposits of legacy sediments (James, 2011; Walter and Merritts, 2008; Merritts et al., 2011, 2013). Census data indicate that by 1840, there were > 65,000 water-powered mills along first to third order streams, every few miles, in the eastern US (Walter and Merritts, 2008).

While many of these small milldams are breached or removed, their upstream reservoirs continue to erode, resulting in highly incised contemporary streams with exposed vertical streambanks that are vulnerable to erosion (Merritts et al., 2011; 2013; Pizzuto and O'Neal, 2009; Wegmann et al., 2012). Not surprisingly, studies have reported anomalously elevated rates of bank erosion and sediment exports from watersheds in the eastern US, undermining stream health (Gellis et al., 2009; Mukundan et al., 2010; Voli et al., 2013; Stewart et al., 2015). Stream-bank erosion has been found to contribute as much as 50-100% of the suspended sediment loads in Piedmont watersheds (Cashman et al., 2018; Gellis et al., 2017; Massoudieh et al.,

2012; Voli et al., 2013; Gellis and Brakebill, 2013). A large fraction of the streambank sediment loadings likely originate from legacy sediments.

Recent work by Cashman et al. (2018) and Gellis et al. (2017) also suggests that in addition to stream banks, stream beds or in-channel storage could also be a significant source of legacy sediments which could be mobilized during storms. Using fallout radionuclides, Gellis et al. (2017) found that 78 of 99 sampled streams in the US Midwest were dominated by (>50%) remobilized channel and bed sediments. Cashman et al. (2018) applied a mass balance approach to an urbanized Mid-Atlantic Chesapeake Bay watershed and found that direct stream bank erosion could only account for 77% of bank-attributed suspended sediment yields, with the remaining 23% attributed to stream bed sediment remobilization. Neither of these studies, however, investigated changes in stream bed sediment composition and potential remobilization over time.

Beyond sediments, even less is known about the nutrient inputs and loadings for carbon (C), nitrogen (N), and phosphorus (P) from stream banks and legacy sediments (Miller et al., 2019). No study to date has investigated what proportion of sediment-bound nutrients can be attributed to upland versus stream bank and legacy sediment sources. Comprised primarily of silt and clay-sized particles derived from rich agricultural soils, legacy sediments may be a significant contributor to watershed nutrient budgets (Inamdar et al., 2017; Walter and Merritts, 2008). Importantly, despite growing recognition of their significance, legacy and stream bank sediments remain unaccounted for in best management practices and watershed modeling efforts (Miller et al., 2019). The omission of legacy sediments from watershed management efforts is exacerbated by a lack of understanding of stream bank contributions to

watershed nutrient yields, as well as how stream bed sediments evolve over time. Given that mitigation and management efforts for upland versus near-stream sediment and nutrient sources could differ substantially (e.g., conservation tillage for upland fields versus stream bank restoration for eroding banks), it is imperative that we correctly identify the sediment and nutrient sources and appropriately target/allocate our limited mitigation and restoration resources.

This study seeks to address these important knowledge gaps in our understanding of legacy sediments and their contributions to contemporary watershed sediment and nutrient yields. Specific questions addressed in this study include:

- 1) What is the contribution of stream bank sediments to watershed sediment and nutrient (C, N, and P) yields, and how do the contributions vary with storm magnitude and seasonal occurrence?
- 2) What proportion of the stream bed sediments are composed of stream banks and other sources and how do they change with time?

We addressed these questions for a fourth order, Mid-Atlantic Piedmont stream located in the Chesapeake Bay watershed. Suspended sediment and nutrient (C, N, and P) concentrations and yields were determined using a combination of high frequency sensor and in-stream sediment sampling. Sediment sources were characterized by sampling upland (forested, agricultural, and urban) and stream banks with legacy sediments. While we did not make a distinction between legacy and non-legacy sediments in the stream banks, we assumed that much of the sediments in banks originated from legacy activities such as mill dams and other impoundments. The Big Elk Creek has a long and extensive history of mill damming with dams every couple of miles along the creek as determined from historic maps. Based on their elemental

and isotopic chemistry, sediments were partitioned into their constituent sources using a recently available sediment unmixing toolbox (Gorman Sanisaca et al., 2017).

## **Chapter 2**

### **LITERATURE REVIEW**

This review provides an overview of the environmental significance of sediments and sediment-bound nutrients in fluvial systems. Specifically addressed are factors influencing stream bank composition and erosion in the Mid-Atlantic region, as well as methods for tracking and quantifying sediment contributions from both upland and channel sources.

#### **2.1 Environmental consequences of sediment and water pollution**

Sediment and sediment-bound pollutants have been identified as the leading cause of water quality impairment in the nation's waterways (USEPA, 2016). Fine sediment, in particular has marked impacts on primary productivity, faunal diversity, and primary producer abundance (Wood and Armitage, 1997). Fine sediment reduces light penetration into aquatic systems, reducing photosynthesis and primary productivity within the stream (Van Nieuwenhuysse and LaPerriere, 1986); reduces the organic content of periphyton cells (Cline et al., 1982); damages macrophyte leaves and stems due to abrasion (Lewis, 1973); and prevents algal cells from attaching to the substrate, as well as smothering periphyton aquatic macrophytes under extreme circumstances (Brookes, 1986). Furthermore, the large surface area and geochemical composition of silt and clay sized sediments make them ideal vectors for other aquatic pollutants, including phosphorus, nitrogen, heavy metals, and other contaminants deleterious to human and aquatic health (Waters, 1995; Wood and Armitage, 1997; Gellis et al., 2016). Sediment-bound nutrients may contribute to the eutrophication of aquatic ecosystems (Waters, 1995; Inamdar et al., 2017). In North America, the cost of

physical, chemical, and biological damage caused by fluvial sediment may be as high \$50 billion, annually (Mukundan et al., 2012).

## **2.2 Total maximum daily loads and sediment sources**

Section 303(d) of the Clean Water Act requires states, territories, and authorized tribes to identify and list impaired water bodies every two years and to develop total maximum daily loads (TMDLs) for pollutants in these water bodies. TMDLs establish the maximum allowable pollutant loadings that a water body can accept and still meet its water quality standards and the Clean Water Act goal of “fishable, swimmable” water bodies (USEPA, 1999). Under the TMDL framework, sediment sources are required to be identified for all water bodies determined to be sediment-impaired.

In the Mid-Atlantic region, major sediment sources include upland sources such as agricultural or forested soils, construction sites, and unpaved road surfaces, as well as near-stream sources such as streambanks, stream beds, and floodplains (Gellis et al., 2009; Walling, 2005). Management strategies to reduce sediment inputs differ depending on the primary sources of sediment – whether the sediment is sourced from upland sources and activities or from near-stream sources. While estimates of sediment yield are available for many water bodies in the US based on stream monitoring, little information is available on primary sources of sediment in many water bodies (Mukundan et al., 2012).

Classified as sediment-impaired in 1998, suspended sediment yields in the Chesapeake Bay watershed are highest in the Piedmont Physiographic Province and lowest in the Coastal Plain, concomitant with steeper topographic gradients and higher erosion rates in the Piedmont compared to the Coastal Plain (Brakebill et al., 2010). A

2010 study attributed 51% of the suspended sediment in the Chesapeake Bay as sourced from agricultural land, 39% from developed areas, 8% from small, non-Coastal Plain tributaries, and 2% from forested areas (Brakebill et al., 2010). The authors, however, did not distinguish what proportion of sediment was derived from upland versus near-stream sources within each category.

### **2.3 Legacy sediments in the Mid-Atlantic region**

In North America, anthropogenic, or legacy sediment, describes the sedimentary deposits produced by the intensive land clearance, agriculture, and mining practices of the early EuroAmerican colonists in North America (James, 2011). These legacy sediments do not occur uniformly over the landscape, but instead collect in certain locations following the natural topography as well as the historical land usage of the region (James, 2011). Recent recognition of the large contributions of legacy sediment to modern sediment budgets has led to reevaluation of major sediment sources in fluvial environments – particularly in the Mid-Atlantic Piedmont Province (James, 2011).

First identified by Walter and Merritts (2008), high stream banks disconnected from the floodplain are ubiquitous throughout the Mid-Atlantic region and are consistent in their stratigraphy: the weathered bedrock valley floor is overlain by a thin (<0.5m) bed of poorly sorted angular to sub-angular gravel, followed by a thin (<0.5 – 1m) bed of dark, hydric, organic-rich silt loam, then a thick (>1m), often laminated sequence of pale to yellowish-brown sequence of fine sand, silt, and clay (Walter and Merritts, 2008; Merritts et al., 2011). Sediments in the basal gravel bed may be cobble or boulder in size and are attributed to colluvial or periglacial processes, as the streams in which they are found are incapable of generating enough shear stress to move

cobbles or boulders as bed load (Merritts et al., 2011). The dark hydric layer is attributed to low-energy wetland environments that existed prior to European settlement, and radiocarbon dating indicates that these soils range in age from 10,500 to 300 years before present (Walter and Merritts, 2008; Voli et al., 2009; Merritts et al., 2011). Lastly, the thick sequence of fine clays and silts is attributed to sediment deposited behind mill dams built by Euro-American colonists in the Mid-Atlantic region.

Vital for grinding grain, fulling wool, producing textiles and paper, cutting wood, making gunpowder, melting and pounding metal, over 65,000 low-head (<7m in hydraulic head) mill dams were built across numerous first- to third-order stream valley bottoms in the Mid-Atlantic region (Merritts et al., 2011). These dams ranged in height from 1.5m to as high as 9m and were especially prevalent in the Piedmont Physiographic Region (Merritts et al., 2011; Merritts et al., 2013). Dam building results in an increase in stream base level and a decrease in water surface slope, and thus a net decrease in water velocity.

These conditions set the stage for extensive sediment deposition in the slack-water ponds created by damming: up to 80% of sediment supplied to dammed streams were retained behind the dams (Merritts et al., 2011). Backwater effects from a single mill dam influence hydrologic conditions several kilometers upstream of the dam itself (Merritts et al., 2011), and the thickness of the accumulated sediment varies depending on the height of the historic dam as well as how far upstream the sediment is from the dam (Walter and Merritts, 2008; Merritts et al., 2011; Merritts et al., 2013). In an archetypical Piedmont watershed with a 60m wide valley and a gradient of 0.002, approximately 180,000m<sup>3</sup> of sediment would be stored up to 2km upstream of a 3m

high mill dam (Merritts et al., 2011). With over 65,000 mill dams built and 5,535 dams built on the Susquehanna River Basin alone (Niemitz et al., 2013), the legacy sediment accumulated behind historic mill dams comprise a major potential source of sediment to Mid-Atlantic watersheds.

This study focuses on the thick fine-grained sediment sequences deposited behind historic mill dams and their contribution to Mid-Atlantic sediment and nutrient budgets, hereafter referred to as stream bank legacy sediments (SBLS) within the context of this study. The chemistry and mineralogy of these historic dam sediments reflect their bedrock and upland soil sources, and are primarily composed of quartz, K-feldspar, kaolinite, and illite (Niemitz et al., 2013). Although these banks typically have low nutrient (carbon, nitrogen, and phosphorus) concentrations (Niemitz et al., 2013; Weitzman et al., 2014), they may potentially still serve as nutrient sources due to the large quantities of sediment supplied to regional watersheds.

#### **2.4 Factors affecting stream bank legacy sediment nutrient concentrations**

Reported mean total carbon and total nitrogen concentrations for legacy sediments in stream banks range from 1.27-1.5% and 0.08-0.17%, respectively (Gellis and Noe, 2013; McKinley et al., 2013; Weitzman et al., 2014). Less data are available for total phosphorus and reactive nitrogen species (nitrate-nitrogen,  $\text{NO}_3\text{-N}$ ) and (ammonium-nitrogen,  $\text{NH}_4\text{-N}$ ). One study reported total phosphorus concentrations ranging from 340 – 958  $\text{mg kg}^{-1}$  (Walter and Merritts, 2008), and another study reported  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  concentrations of 4  $\text{mg kg}^{-1}$  and 3  $\text{mg kg}^{-1}$ , respectively (Weitzman et al., 2014).

Sediment elemental and nutrient concentrations are ultimately derived from their geologic source material (Pulley et al., 2017). Nutrient concentrations, however,

may further be influenced by both biological processes and physical processes. Nitrifying bacteria are obligate autotrophic aerobes that convert  $\text{NH}_4^-$  to  $\text{NO}_3^-$  via oxidation. Denitrifying bacteria are obligate heterotrophic anaerobes that convert  $\text{NO}_3^-$  to unreactive molecular nitrogen gas ( $\text{N}_2$ ), consuming carbon (C) in the process (Weil and Brady, 2017). One study found high potential nitrification and denitrification rates in near-surface legacy sediment banks. The aerobic, unsaturated conditions present in surface sediments, however, promote nitrification over denitrification, consistent with the study's findings of ammonium consumption along the vertical bank profile. The authors concluded that surficial legacy sediment soils may serve a source of  $\text{NO}_3^-$  to watersheds, although data from their watershed were inconclusive on how much stream banks contributed to watershed N budgets (Weitzman et al., 2014).

Sediment-associated phosphorus (P) primarily exists in three forms: solution P, active P, and fixed P, but never as elemental P (Fox et al., 2016). Solution P is typically present as orthophosphate and is bioavailable for plant uptake; active P is solid P that is readily soluble in water and replenished by solution P pools; fixed P exists as insoluble inorganic compounds and does not contribute watershed P budgets (Fox et al., 2016). Active and solution P pools are influenced by biological uptake as well as sorption/desorption processes occurring along the sediment-water interface. The latter processes are especially important in controlling legacy sediment P concentrations as chemical fertilizers containing 100% water soluble organic P are liberally applied on agricultural fields in excess of plant needs; the surplus P is then transported either directly to streams or sorbed onto sediments.

Rates of P sorption onto sediments, legacy or otherwise, are influenced by P forms, pH, alkalinity, iron (Fe) and aluminum (Al) oxides, mineralogy, and organic

matter (Fox et al., 2016). Studies in the Midwest have demonstrated that stream banks are a significant, if not major source of P to watersheds (Miller et al., 2014; Purvis et al., 2016). Little to no research, however, has investigated the potential contribution of mill pond and bank legacy sediments to nutrient budgets in the Mid-Atlantic region, nor the role of different erosive processes in mobilizing sediment-bound nutrients to streams (Miller et al., 2019). This study seeks to address these knowledge gaps.

## **2.5 Processes influencing stream bank legacy sediment erosion**

Stream bank legacy sediments are mobilized into the watershed through a combination of fluvial and subaerial erosive processes. Following conceptual channel evolution models and geomorphic studies of dam failure, fluvial erosion dominates immediately after dam-breach as the stream cuts down through unconsolidated sediment and generating a knickpoint (Doyle et al., 2003; Evans et al., 2007). Vertical channel incision continues until the stream reaches the base of the original valley, and the knickpoint propagates through sediment reservoirs until the entirety of the dam-impacted reach has become graded to the new local base level (Merritts et al., 2013). The result is a deeply incised channel with high stream banks that are disconnected from both the floodplain and groundwater sources. All sediment eroded as the channel seeks to return to its original base level is mobilized into the channel.

Following the definitions put forth by Lawler et al. (1997), stream bank erosion is driven by three main processes after the channel has reached its original base level (Merritts et al., 2013):

1. subaerial processes: drying-wetting, freeze-thaw cycles;
2. mass wasting: bank failure via collapse, calving;

3. fluvial entrainment: detachment and entrainment of sediment by flowing water.

Couper (2003) found that stream banks with high silt-clay content were particularly vulnerable to subaerial erosive processes as well as a vertical zoning of erosive processes: lower portions of the bank in contact with streamflow were susceptible to fluvial erosion, and upper portions of the bank were most susceptible to subaerial processes such as drying/wetting cycles and freeze/thaw cycles.

Subaerial processes weaken bank cohesive strength and reduce the critical shear stress required to mobilize sediment from banks into the channel, increasing the susceptibility of bank sediment to fluvial erosion (Wynn, 2006; Merritts et al., 2013). Freeze-thaw processes are especially important in the Mid-Atlantic region: one study found that net erosion was highest during the Winter due to freeze-thaw processes, with 85% of bank erosion over a two-year study period occurring during the Winter (Wolman, 1959); this study site was later identified as being immediately upstream of a breached mill dam (Merritts et al., 2013). Freeze-thaw processes reduce bank cohesive strength due largely to the formation of needle ice (Wolman, 1959; Gatto, 1995; Couper, 2003), and more recent studies have found that intense Winter rainfall combined with freeze-thaw cycles contributed to a significant portion of annual watershed sediment and particulate nutrient yields in a small forested headwater Piedmont catchment (Inamdar et al., 2017).

## **2.6 Comparisons of Mid-Atlantic sediment budgets and contributions from legacy sediments**

Five major physiographic provinces supply water and sediment to the Chesapeake Bay: the Appalachian Plateau, the Blue Ridge, the Coastal Plain, the

Piedmont, and the Valley and Ridge (Gellis et al., 2009). Annual sediment yields for these regions obtained from USGS gauging stations are presented in Table 2.1 (Gellis et al., 2005):

Table 2.1: Average annual sediment yields for different physiographic regions from 65 USGS gauging stations in the Chesapeake Bay watershed from 1952-2001. Watersheds draining multiple physiographic provinces are classified under the province that contributes the largest drainage area. Adapted from Gellis et al., 2005.

<b>Province</b>	<b>Annual sediment yield (kg ha<sup>-1</sup> yr<sup>-1</sup>)</b>
Appalachian Plateau	588
Blue Ridge	568
Valley and Ridge	663
Piedmont	1037
Coastal Plain	119

Sediment yields are, on average, lowest in the Coastal Plain and highest in the Piedmont. Low sediment yields in the Coastal Plain are attributed to a higher frequency of overbank flows (inducing floodplain sediment deposition), flatter hydrographs, longer periods of inundation, and high rates of riparian sediment retention (Gellis et al., 2009); flatter stream slopes result in lower stream velocities and thus smaller channel shear stresses for sediment mobilization and transport. Sediment yields during the period studied (1985-2001) in Gellis et al. (2009) were particularly high in the Conestoga River watershed, a tributary of the Susquehanna River – the same watershed where the role of mill dams in the creation of high stream banks was first discovered (Walter and Merritts, 2008).

Numerous studies have investigated sources of suspended sediment to watersheds along the East Coast of the US (Table 2.2). These studies are primarily

focused on storm-mobilized sediment, as storms are responsible for contributing a substantial proportion of annual sediment and nutrient exports to watersheds (Inamdar et al., 2017).

Table 2.2: Comparison of stream bank contributions to storm suspended sediments from selected studies in the Mid-Atlantic region.

<b>Study</b>	<b>Watershed</b>	<b>Dominant land-use</b>	<b>Geographic setting</b>	<b>Sediment sources</b>	<b>Avg. bank contribution</b>
Gellis et al., 2009	Pocomoke River, MD (157 km <sup>2</sup> )	Agricultural	Mid-Atlantic Coastal Plain	Stream banks, stream beds & ditches, cropland soils, forested soils	7%
Gellis et al., 2009	Mattawoman Creek, MD (134 km <sup>2</sup> )	Agricultural	Mid-Atlantic Coastal Plain	Stream banks, construction sites, cropland soils, forested soils	31%
Gellis et al., 2009	Little Conestoga Creek, PA (110 km <sup>2</sup> )	Agricultural/ Urban	Mid-Atlantic Piedmont	Stream banks, construction sites, cropland soils	23%
Mckinley et al., 2012; Mukundan et al., 2010	North Fork Broad River, GA (182 km <sup>2</sup> )	Forested	Southern Piedmont	Stream banks, subsurface, pasture	68% - 80%
Voli et al., 2013	Four catchments within the Falls Lake, NC watershed totaling 150 km <sup>2</sup>	Urban to forested	Southern Piedmont	Stream banks, roads (paved and unpaved), construction sites, forested soils	62%, 58%, 33%, 27%
Massoudieh et al., 2013	Mill Stream Branch, MD (31.6 km <sup>2</sup> )	Agricultural	Mid-Atlantic Coastal Plain	Stream corridor, croplands, forests	94%
Gellis & Noe, 2013	Linganore Creek, MD (147 km <sup>2</sup> )	Agricultural	Mid-Atlantic Piedmont	Stream banks, cropland soils, forested soils	53%
Cashman et al., 2018	Upper Difficult Run, VA (14.2 km <sup>2</sup> )	Suburban	Mid-Atlantic Piedmont	Stream banks, forested soils, roads	87%

Gellis et al. (2009) include three such studies with sediment source estimates presented as sediment weighted averages. The first of these studies was conducted in

the Pocomoke River watershed near Willards, MD on the Coastal Plain. For seven storm events from 2001 through 2003, an average of 7% of event suspended sediment came from stream banks, 34% from stream bed and ditches, 46% from cropland soils, and 13% from forested soils. The second study was conducted within the Mattawoman Creek watershed near Pomonkey, MD in the Coastal Plain. Here, for six events in 2004, 31% of suspended sediment came from banks, 23% from construction sites, 17% from cropland soils, and 29% came from forests. Suspended sediment concentrations (SSC) were relatively low for both watersheds, with SSC values typically not exceeding 100 mg/L, even during high flow events (Gellis et al., 2009).

The third study was conducted at the Little Conestoga Creek near Millersville, PA in the Piedmont Physiographic Province. Event SSC values were much higher in this watershed, with 59% of suspended-sediment samples exceeding 100 mg/L up to a maximum SSC of 1400 mg/L. Despite cropland only constituting 13% of the watershed, 100% of analyzed suspended sediment was attributed to cropland soils for 10 of the 12 sampled events from 2003-2004; 98% and 100% of suspended sediment was attributed to bank sediments for the remaining two events (Gellis et al., 2009).

Other sediment source studies conducted in Piedmont watersheds report more consistent contributions from stream banks. Two studies conducted in the North Fork Broad River watershed in the Southern Piedmont region of Georgia tracked sediment source contributions at discrete intervals of event hydrographs for 35 events from 2008-2011 (Mukundan et al., 2010; Mckinley et al., 2013). About 60% of all suspended sediment was attributed to stream bank sources, on average, with contributions ranging from 40-80%. Furthermore, by collecting discrete sediment samples, the authors were able to discern that stream bank contributions were greatest

around peak flow and on the falling limb of the hydrograph; cropland, human impacted, and forested soils comprised a plurality during the rising limb (Mukundan et al., 2010; Mckinley et al., 2013).

Further north, another study (Voli et al., 2013) compared sediment source contributions in four small tributaries within the Falls Lake catchment, located in the Piedmont region of North Carolina. Three of the watersheds were classified as impaired under the Clean Water Act, and the fourth was largely undeveloped and the only watershed to contain historic records of mill dams. On average, 27% to 58% of the suspended sediment exports in the three impaired watersheds were attributed to stream banks, with the rest attributed to forested soils, paved roads, and construction sites; contributions from construction sites were highest in the watersheds closest to and most impacted by the city of Durham. In the undeveloped, mill dam-impacted watershed, 62% of the suspended sediment flux was attributed to stream banks – higher than the three watersheds without a record of historic mill dams (Voli et al., 2013).

Two other sediment source apportionment studies were conducted in tributaries of the Chesapeake Bay. The first was conducted in the agriculture and forest-dominated Linganore Creek watershed, Maryland. For 36 storm events from 2008 to 2010, 53% of the annual suspended sediment load was attributed to stream banks, 44% to agricultural soils, and 3% to forested soils (Gellis and Noe, 2013). Stream bank contributions were highest during Winter events, corresponding to increased erosion rates induced by freeze-thaw and other subaerial processes (Wolman, 1959; Gatto, 1995). The authors also highlight the importance of temporary storage in sediment studies, an aspect neglected in other sediment source tracking

studies – sediment collected during a storm event may not necessarily have been eroded and transported during that event (Skalak and Pizzuto, 2010). Rather, sampled sediment is more likely to have been eroded by previous storms and held in channel storage for a period of time before being remobilized and collected during a select event (Gellis and Noe, 2013).

The second study was conducted at Mill Stream Branch, Maryland, a small tributary of the Chesapeake Bay situated entirely within the Coastal Plain Physiographic region. Although agriculture comprised the dominant land use in the watershed, 95-100% of the suspended sediment collected from five storms in 2009 were attributed to stream banks (Massoudieh et al., 2012). The authors suggest that low sediment contributions from agriculture are due to riparian forests and floodplains buffering upland agricultural erosion; eroded agricultural sediments are trapped and redeposited onto forested floodplains, consistent with the observations of Gellis et al. (2009). The authors further observe that overland flow is necessary to erode and transport upland sediment, and they are unclear if overland flow occurred during the five sampled events (Massoudieh et al., 2012).

While these studies highlight the importance of stream bank and channel contributions to Mid-Atlantic sediment exports, none address the potential for stream banks to contribute to Mid-Atlantic nutrient exports. Furthermore, studies have neglected to ascertain how seasonal, antecedent moisture, and precipitation conditions influence suspended sediment sources.

## **2.7 Sediment source apportionment via geochemical sediment fingerprinting**

Beginning as simple qualitative estimates in the 1970s, suspended sediment source apportionment studies are vital in identifying targets for remediation (Collins et

al., 2016). Statistical methods were introduced in the 1990s to provide more robust, qualitative information on sediment sources and from there, it became apparent that single tracer studies could not reliably differentiate between multiple potential sediment sources (Collins et al., 2016). The modern approach is referred to as sediment fingerprinting, and is based on two assumptions: first, that potential sediment sources within a watershed can be discriminated, or “fingerprinted” by different diagnostic physical and chemical properties or tracers, and second, that comparing the properties of collected suspended sediment with those of potential sources permits the relative contribution of each source to be assessed: event-generated suspended sediment is assumed to be a linear mixture of sediment from potential sediment sources within the watershed (Walling et al., 1999; Collins et al., 2016).

Sediment fingerprinting first entails the identification of the target sediment fraction followed by the identification of potential sediment sources within a watershed. As the “fingerprint” tracers often vary as a function of particle size and specific surface area, common practice in sediment fingerprinting studies is to fingerprint only the <63  $\mu\text{m}$  fraction of sediment as it comprises the dominant proportion of suspended sediment in most fluvial systems and limits the effects of particle size on tracer concentrations (Collins et al., 2016; Laceby et al., 2017). Tracer concentrations generally increase with decreasing particle size, although particle size effects may not be linear or consistent between tracers and sediment lithology (Koiter et al., 2018).

Classification of sediment source groups is typically conducted prior to the study based on management or research goals. For example, a study seeking to identify targets for remediation and best management practices may classify sediment

sources based on land usage, whereas a study seeking to quantify sediment contributions from different erosive processes may classify sediment sources by whether they are surface or subsurface sources (Collins et al., 2016). The majority of fingerprinting studies fall into the former category and classify sediment source groups by land usage, despite research suggesting that the impacts of land usage on potential tracer properties are superseded by the impacts of local geology and/or soils on tracer properties (Collins et al., 2016; Pulley et al., 2017).

Classifying sediment sources by land usage in watersheds with variable geology and/or soils is likely to result in sediment source groups with large amounts of within-group tracer variability, increasing uncertainty in the resulting source apportionment models (Pulley et al., 2017). Wilkinson et al. (2015) and van der Waal et al. (2015) approached the issue by emphasizing source samples collected from heavily eroding areas and key erosional features, respectively. These approaches, however, require an advanced understanding of the connectivity between sediment sources and the channel that may not be available in all watersheds (Collins et al., 2016).

Alternatively, Walling and Woodward (1995) applied cluster analysis to classify source groups based on pre-selected tracers. Similarly, Pulley et al. (2017) used tracer signatures in a principal component analysis (PCA) and cluster analysis to determine the grouping of surface and subsurface sources that simultaneously minimized within-group tracer variability while retaining management-targeted source groups. Sediment samples are then collected from each source group to construct a sediment “fingerprint” that encompasses the full range of natural variability within the source sediments. Samples are typically a composite of samples taken from the upper

few centimeters of the soil profile, corresponding to the typical depth that sediment generation processes operate at (Collins et al., 2016).

As sediment source apportionment studies are typically focused on event-generated suspended sediments, target sediment for source apportionment may be collected as instantaneous samples collected as discrete points on an event hydrograph (Collins et al., 2012; Mckinley et al., 2012); as time-integrated samples comprised of suspended sediment from entire events (Massoudieh et al., 2012; Voli et al., 2013); or historical floodplain, lake, and channel deposits to reconstruct changes in sediment sources over time (Mukundan et al., 2012; Walling and Foster, 2016). Discrete samples are typically collected with automated samplers or mobile pumped centrifuges (Mckinley et al., 2012), time-integrated samplers with sediment traps installed within the channel (Phillips et al., 2000), and historic deposits with sediment corers (Collins et al., 2016).

Both source and target samples are then analyzed for a suite of tracer properties suspected to be temporally and spatially conservative, significantly between different source groups, and insignificantly different within source groups. Differences in sediment tracer concentrations are driven by interactions of sediment source material, climate, hydrology, vegetation, soil age, weathering properties, and human activity (Koiter et al., 2013). The fundamental assumptions behind sediment fingerprinting are founded on the basis that select tracer properties behave conservatively or vary predictably during sediment erosion, transport, and deposition, such that source and target sediments can be directly compared (Collins et al., 2016). Tracers that have been successfully applied to sediment fingerprinting studies include geochemical properties such as inorganic elements, radionuclides, and mineral

magnetism, biochemical properties including C, N, P,  $\delta^{15}\text{N}$ , and  $\delta^{13}\text{C}$ , and physical properties including sediment color, mineralogy, and particle size (Foster and Lees, 2000; Gellis and Noe, 2013; Koiter et al., 2013; Collins et al., 2016). These tracers may not necessarily be conservative in all circumstances and in all watersheds, however.

Fallout radionuclides, for instance, are non-conservative by definition due to radioactive decay; furthermore, naturally occurring radionuclides such as  $^7\text{Be}$ ,  $^{10}\text{Be}$ , and  $^{210}\text{Pb}$  are continuously being deposited on the landscape and changing environmental concentrations. Mineral magnetic properties are strongly susceptible to variations in sediment particle size, organic matter content, as well as microbial processing (Collins et al., 2016). Inorganic elemental properties are similarly susceptible to particle size and organic matter variations, and may further be affected by ion exchange, adsorption/desorption, precipitation/dissolution, complexation, and microbial uptake. Biochemical tracers such as C, N, P,  $\delta^{15}\text{N}$ , and  $\delta^{13}\text{C}$  are biochemically active, and thus tracer properties may be modified by both biological and physical processes. Any or all of these processes may not disqualify a tracer from consideration in fingerprinting studies, so long as the processes occur over longer timescales than that of the fingerprinting study (Koiter et al., 2013).

As comprehensive investigations into how biogeochemical and physical processes alter sediment properties across the landscape and through fluvial networks do not yet exist, tracers are assumed to be conservative if target tracer concentrations fall within the minimum and maximum range of source tracer concentrations (Gellis and Noe, 2013; Koiter et al., 2013; Collins et al., 2016). A majority of sediment fingerprinting studies apply simple methods to account for non-conservative tracer

behavior: particle size and organic matter effects on tracer concentrations are typically corrected for through simple linear regressions. Recent research, however, suggests that these corrections may introduce more uncertainty into unmixing models as particle size and organic matter effects are often non-linear and non-consistent between different sediments (Koiter et al., 2013; Laceby et al., 2016).

After sediment collection and analysis, sediment source apportionment models are then determined quantitatively through least squares mass balance regressions (Collins et al., 1997; Collins et al., 2010; Gellis and Noe, 2013) or through Bayesian approaches (Massoudieh et al., 2012; Cooper et al., 2014). The least squares approach uses a suite of tracers to determine a discrete solution of percent contributions from each source group that simultaneously minimizes the sum of squared residuals. Estimates of uncertainty are obtained through Monte-Carlo simulations, where the mixing model is run >1000 times with a single random source sample removed from each source group. The mixing model results from the Monte-Carlo simulation should be similar to the results of the model results from the entire dataset (Gorman Sanisaca et al., 2017).

Bayesian approaches, in contrast, are a probabilistic approach in which sediment source contributions are derived from tracer concentrations in each source area multiplied by the proportional sediment contribution from that source. Results are presented as a range of potential contribution percentages in the form of probability density functions, encompassing both the estimated likeliest source contributions as well as estimates of uncertainty. The Bayesian approach is less prone to misidentifying target sediment as solely derived from one source group than the least squares approach (Cooper et al., 2014).

## **2.8 Channel sediment storage and remobilization**

Gellis and Noe (2013) observed one key limitation of the sediment fingerprinting approach: target sediment collected and fingerprinted for a given storm may not necessarily have been eroded, transported, and collected during that event. While stream bank material is readily eroded and entrained due to its channel proximity, upland sediment is likely to undergo multiple deposition, erosion, and transport cycles before its ultimate delivery into the channel. Sediment may further enter storage once transported into the channel. A study by Skalak and Pizzuto (2010) found that sediment could become trapped behind woody debris and remain in storage for decades. Other studies observe that 8 to 12% of suspended sediment from all sources could be stored in floodplains for long periods prior to remobilization (Schenk et al., 2013; Pizzuto et al., 2016).

These studies highlight the importance of considering sediment storage in fingerprinting studies as well as the factors contributing to sediment storage in watersheds. Schenk et al. (2013) created bank and floodplain budgets for three Piedmont streams and observed that floodplains served as net sediment sinks in two watersheds and as a sediment source in the third. They found that the ratio of channel width to floodplain width was well correlated with the potential floodplain sediment trapping. Pizzuto et al. (2016) observed high floodplain sedimentation rates in a watershed with low (~1.5m) stream banks and a high frequency of overbank flood events: 56% of the 100-year floodplain is inundated every two years, and 83% of the floodplain is inundated every five years. These conditions may not be present in all watersheds – watersheds with high streambanks and low overbank flood event frequencies may not experience much sediment trapping.

Recent studies by Cashman et al. (2018) and Gellis et al. (2016) suggest that a significant proportion of fluvial suspended sediment is attributed to remobilization of sediments in channel storage. Using fallout radionuclides as proxies for sediment age, Gellis et al. (2016) found that fine suspended sediment samples from 78 of 99 sampled Midwestern watersheds were dominated by (>50%) channel-derived sediment; the remainder of the suspended sediments were attributed to surface sediments less than 100 days old. These results are consistent with the observation that surface-derived fine-grained suspended sediment moves rapidly through watersheds, and applicable to the Mid-Atlantic region as streams in both the Mid-Atlantic and the Midwest suffer from deeply incised channels and high stream banks (Walter and Merritts, 2008; Miller et al., 2014).

Cashman et al. (2018) conducted a sediment fingerprinting study in the Upper Difficult Run watershed in Fairfax County, Virginia, and found that both stream bed and fine suspended sediments were dominated by stream bank inputs (98% and 91%, respectively). From watershed sediment budgets, they determined that direct bank erosion rates were insufficient to account for the suspended sediment load attributed to stream banks, without accounting for remobilization of bank-derived sediment from channel storage. This study, however, only collected three stream bed samples from a single sampling session (Cashman et al., 2018), and thus the authors were unable to characterize any changes in stream bed composition over space or time.

## **2.9 Broader watershed and environmental challenges**

In 2010, the U.S. EPA established a plan for Chesapeake Bay pollutant load reduction and restoration called the Chesapeake Bay Total Maximum Daily Load program (Bay TMDL), with the goal of accomplishing 100% of the reduction and

restoration targets by 2025, and 60% of the targets by 2017. By 2018, it was reported that the 60% reduction targets had been met for phosphorus and sediment, but not for nitrogen (USEPA, 2018). These reductions were largely accomplished through pollutant load reduction from readily identifiable sources such as agriculture, stormwater, and wastewater treatment plants through the implementation of best management practices (BMPs) and stream restoration (USEPA, 2018).

Legacy and in-channel pollutant generation, however, has largely been excluded from both the BMPs and the stream restoration projects in the Chesapeake Bay. The BMPs were designed and implemented based on the Phase 5 Chesapeake Bay Watershed Model which did not explicitly consider legacy and channel sediments (USEPA, 2010; Chesapeake Bay Program, 2018) Stream restoration projects are similarly problematic. An estimated one billion USD is spent on domestic stream restoration projects annually (Bernhardt et al., 2005), with a 2005 study estimating that at least 400 million USD had been spent on restoration projects within the Chesapeake Bay Watershed (Hassett et al., 2005). Despite the amount of money spent, restoration projects do not typically consider nitrogen reductions (Craig et al., 2008), and frequently suffer from poor documentation (Bernhardt et al., 2005), insufficient pre- and post-restoration monitoring (Hassett et al., 2005; Buijse et al., 2002), or, in some cases lack a sound scientific underpinning altogether (Buijse et al., 2002)

The work of Walter and Merritts (2008) suggests that the stream geomorphic based restoration projects that are popular in the Mid-Atlantic may not be reaching their full effectiveness as they do not address contributions from stream bank legacy sediments. With readily identifiable pollutant sources (primarily upland) already regulated, meeting 2025 Bay TMDL reduction targets may not be possible without

stream restoration projects designed specifically to address legacy sediments and nutrients (Craig et al., 2008; Richardson et al., 2011).

## **Chapter 3**

### **METHODS**

#### **3.1 Site Description**

This study was performed in the Big Elk Creek, a 164 km<sup>2</sup> (63 mi<sup>2</sup>) Chesapeake Bay watershed, draining parts of Chester County, Pennsylvania; New Castle County, Delaware; and Cecil County, Maryland (Figure 3.1). The watershed is underlain by the Mt. Cuba Wissahickon Formation and includes pelitic gneiss, pelitic schist, with subordinate amphibolite and pegmatite (Blackmer, 2005). Soils in the study primarily comprise deep, well-drained Glenelg-series soils on nearly level to moderately steep soils. Hill-slope soils are coarse loamy, mixed, mesic Lithic Dystrudepts, and valley bottoms are comprised of Oxyaquic Dystrudepts due to seasonal water saturation (NRCS, 2019). Mean annual temperature and precipitation for the region are 13°C and 1119 mm, respectively (WRCC, 2019).

Land usage within the Big Elk Creek Watershed is 25% developed (primarily suburban and low development), 29% forested, 42% agricultural, and <3% wetlands (NLCD, 2011). Sample collection and field work were conducted at three primary field sites located within the Fair Hill Natural Resource Management area located in Cecil County, MD to track changes in stream bed and storm suspended sediment composition over time along the river continuum. Two sites are located along the main stem of the Big Elk Creek and the third site is located at the mouth of a 79 ha headwater tributary of the Big Elk Creek (Figure 3.1). The Big Elk Creek upstream site is located just upstream of the confluence between the 79 ha tributary and the Big Elk Creek. Locations of the sampling sites are presented in Table 3.1.

Both the main stem sampling sites (Figure 3.1) are immediately upstream (within 100 m) of now breached mill dam locations (some dam remnants still exist at the downstream site). At least two mill dams existed between our two study locations on the main stem of Big Elk creek and numerous other dams were located every few kilometers on the Big Elk Creek (Historic Map Works, 2019). Visual surveys for the study reach indicate large deposits of legacy sediments in the valley-bottoms and stream banks. The legacy sediment profiles in the banks are revealed by their nearly-horizontal layering (a result of deposition behind dams, e.g., see Merritts et al., 2011) and light-colored silty/clayey sediments occasionally intermixed with sand lenses that overlay darker organic horizons or leaf layers, potentially pre-colonial in age. Our carbon dating ( $^{14}\text{C}$  age, unpublished data) of the buried leaf layer at the downstream Big Elk Creek sampling site revealed a mean age of  $\sim 220$  years, confirming that the overlying sediments were deposited over the past 200 years.

Table 3.1: Drainage area, latitude, and longitude of the three primary field sites.

Site	Drainage Area (km <sup>2</sup> )	Location (Lat, Long)
79-ha tributary	0.79	-75.84, 39.72
Big Elk Creek upstream	114	-75.84, 39.71
Big Elk Creek downstream	122	-75.83, 39.69

### 3.2 Discharge, suspended sediment yield, and erosion monitoring

Precipitation data were obtained from a weather station administered by the Delaware Environmental Observing System (DEOS) is located half a kilometer away from the Big Elk Creek upstream site. Streamflow stage and discharge were available from a USGS gaging station (USGS 01495000, drainage area of 133 km<sup>2</sup>) located two miles downstream from the Big Elk Creek downstream site. Stream turbidity in

Formazin Nephelometric Units (FNU) were taken every half hour with an in-situ YSI EXO2 sonde deployed at the Big Elk Creek upstream site.

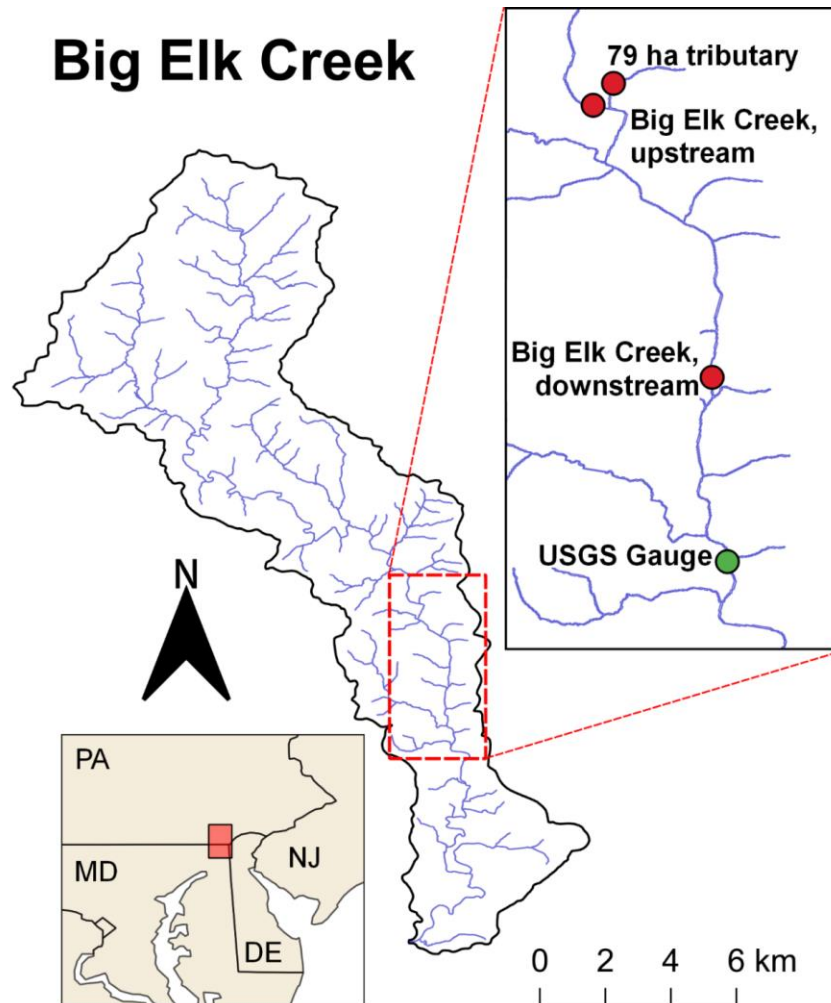


Figure 3.1: The location of the study watershed across Pennsylvania (PA), Maryland (MD), and Delaware (inset, left). The location of the three suspended sediment sampling sites are indicated by red circles and the USGS gauging station (01495000) with a green circle. The drainage areas for the three sampling sites were 0.79 km<sup>2</sup> (tributary of Big Elk Creek), 114 km<sup>2</sup>, and 122 km<sup>2</sup> (located along the main stem of the Big Elk Creek).

A relationship between stream turbidity measurements and actual suspended sediment concentration (SSC) along with the USGS discharge information was used to calculate storm and annual suspended sediment yields (Figure A1). Discrete storm samples were manually collected in 250mL HDPE bottles during storm events at the location of the EXO2 sonde and filtered through 0.7 $\mu$ m pre-combusted glass fiber filters (Sterlitech, B0064SFI0E) to determine suspended sediment concentrations. Discrete samples were collected from the left, center, and right of the channel to verify that suspended sediment loads were laterally homogeneous during high flow events. Turbidity data were not available for approximately two weeks in June 2018 due to sensor issues, and neither suspended sediment nor storm nutrient yields were determined for the June 11, 2018 storm event.

To provide some estimate of bank erosion and to compare against values from sediment fingerprinting, two sets of four erosion pins were installed along the banks of the Big Elk creek, one set each at the upstream and downstream field sites. The 1.2 m (48") long steel pins were driven into the banks to a uniform exposed length of 15.2 cm (6") on August 3, 2017. Pins were installed at 0.2, 0.7, 1.5, and 2.3 m from the bottom of the stream bank at the upstream site, and 0.4, 0.74, 1.3, and 1.7 m from the bottom of the stream bank at the bottom site. These pins were monitored during weekly field excursions to the watershed and measured after potential erosive events. Erosion pin data are presented in mean change in exposed pin length since installation in cm, averaged from both sets of pins for each measurement date. Measurements could not be made of the bottom-most pin at either site on January 7, 2018 due to the pins being frozen underwater, nor at the bottom-most pin at the downstream site on May 25, 2018 due to the pin being covered by deposited sediment. We have set the

latter measurement to be zero for the purpose of taking an average and for further calculations.

### **3.3 Source Sediment Sampling**

A total of 10 stream banks were sampled with a clean trowel for bank sediments in fall and Winter of 2017-2018. Five of these 10 banks were identified as stream bank legacy sediments located immediately adjacent to breached mill dams and sampled at multiple depths to characterize the variability of stream bank chemistry with depth. The five other banks were sampled as bulk samples obtained by vertically scraping the outermost 2 cm of the bank surface and thus integrating the sediment chemistry variability with depth. Twenty-three bank sediment samples were collected in total.

Upland sediment source groups were defined based on land use since the geology of the watershed was fairly uniform (Blackmer, 2005). Land use classifications were based on NLCD (2011) maps and differentiated into agricultural (including both pasture and cropland) soils, forested soils, and “developed” sediments. As the developed areas upstream of the field sites were largely impervious in nature, developed end-member sediments were taken from unpaved gravel roads and sediment accumulated on bridges crossing the Big Elk Creek.

Sampling locations for each source group were identified based on their proximity to erosional features such as rills or gullies through a 1 m-resolution digital elevation model in QGIS 2.18.11 (QGIS Development Team, 2019). Upland source samples were then collected from the upper 2 cm of the soil surface with a clean trowel following the methods of Gellis and Noe (2013) - only the top 2cm was collected to emulate the soil that would potentially be eroded and transported to the

stream network during storm events. Each sample was a composite of five samples taken from within an approximate 5m radius to minimize localized variation in soil properties. Twenty-four upland source samples were collected altogether, comprising 11 agricultural soil samples (six cropland, five pasture), seven forested soil samples, and six “developed” soil samples.

### **3.4 Storm suspended sediment sampling**

Storm mobilized suspended sediments were collected from the three stream sampling sites (Figure 3.1) using passive samplers. These samplers were modified from Johnson et al. (2017) and were designed to collect a representative storm composite of sediment over the duration of an event. The samplers were constructed from 4” (~10cm) diameter Schedule 40 PVC pipe, each sampler stood 0.6 m above baseflow with 2 mm slits on the upstream face to collect suspended sediment and holes on the downstream face to drain excess water. Samples were retrieved within 24 hours of the end of each sampled storm event. Ten storm events varying in rainfall amount/magnitude, duration, and timing were sampled and studied over August 2017 to 2018. Samplers did not collect enough material during the October 30, 2017, January 12, 2018, and June 11, 2018 events from the 79-ha tributary to fingerprint. No sediments were collected from the January 12, 2018 event at the downstream site as the sampler was destroyed by ice floes. The three events in February 2018 and the two events in May 2018 events occurred in succession, and samples from these events were collected after stage levels had receded and before the onset of another event.

### **3.5 Stream bed sampling**

Stream bed sediment samples were collected from the three stream sampling sites at the end of every month from November 2017 to November 2018. Bed samples were collected from the upper 2 cm of the stream bed and each individual sample was further a composite of five samples within a 5 m radius. Care was taken to minimize both collection of suspended sediment and loss of bed sediments to suspension, and further to ensure that samples were collected from approximately the same location within the watershed. No stream bed samples were collected in December 2017 as all sampling sites were frozen over. All collected samples were kept on ice in the field and frozen upon return to the University of Delaware. Stream bed sediments were generally coarse-grained (>90%) in nature, and seven stream bed samples did not have enough fine sediment for the full suite of chemical analyses and were thus not used in sediment fingerprinting.

### **3.6 Laboratory Analyses**

Source and storm composite samples were air-dried at 20°C, disaggregated with mortar and pestle, and dry-sieved into coarse ( $\geq 63 \mu\text{m}$ ) and fine ( $< 63 \mu\text{m}$ ) size fractions. The fine fractions were then submitted to the University of Delaware Soils Testing Lab (UDSTL) and the Central Appalachians Stable Isotope Facility (CASIF) for subsequent elemental and stable isotope analyses, respectively. Analyses were limited to the fine sediment fractions as they comprise most of suspended sediment in fluvial systems (Collins et al., 2016).

Fine sediments were analyzed for 16 elements and inorganic nitrogen concentrations at the UDSTL. Eleven of the 16 elements (P, K, Ca, Mg, Mn, Mg, Zn, Cu, Fe, B, S, Al, Si) were extracted through Mehlich-3 digestion (Mehlich, 1984).

Heavy metals and total phosphorus (As, Cd, Co, Cr, Cu, Ni, P, Pb, Zn) were obtained through microwave-assisted acid digestion (USEPA, 2007). Digestates were then analyzed using inductively coupled plasma optical emission spectrometry; Cu, P, and Zn concentrations were determined for both the Mehlich-3 and EPA3051 digestates. Mehlich-3 extracted elements are henceforth denoted with the M3- prefix. Both microwave-digested and M3-extracted P were considered in this study, with M3-P comprising the more bioavailable and labile fraction of P in sediments (Sims et al., 2002). Nitrate (NO<sub>3</sub>-N) and ammonium (NH<sub>4</sub>-N) were determined at the UDSTL via KCl extraction.

Samples were then analyzed for total carbon, total, nitrogen, and stable isotopic ratios of carbon (<sup>13</sup>C/<sup>12</sup>C) and nitrogen (<sup>15</sup>N/<sup>14</sup>N) at the CASIF. Carbon isotopic ratios are presented as δ<sup>13</sup>C, reported in per mill <sup>13</sup>C relative to Vienna Pee Dee Belemnite, and nitrogen ratios as δ<sup>15</sup>N, reported as per mill <sup>15</sup>N relative to atmospheric N<sub>2</sub>.

### **3.7 Sediment Fingerprinting and Source Apportionment**

Sediment fingerprinting and source apportionment were conducted with the SEDiment Source Assessment Tool (Sed\_SAT), a publicly available comprehensive toolbox for sediment fingerprinting (Gorman Sanisaca et al., 2017). Inputs to Sed\_SAT are the identified source sediments and the target samples to be unmixed: stream beds and storm suspended sediments in our case. Both source and target sample tracer data are first preprocessed by checking for data completeness, and either removing or imputing non-detects and missing data; source sample classification is determined by user input. Arsenic (As) and cadmium (Cd) were removed at this step due to data incompleteness. Total C, total N, total P, M3-P, NH<sub>4</sub>-N, and NO<sub>3</sub>-N were

also removed from consideration due to their inherently reactive and non-conservative nature.

Source data were then tested for outliers, corrected for grain size and organic content if available, and tested for conservative behavior with a bracket test: whether target tracer concentrations fall within the minimum and maximum bounds of source tracer concentrations ( $\pm 10\%$  to account for instrumental uncertainty). We chose not to include particle size or organic matter corrections as these corrections may introduce more uncertainty into fingerprinting results, and organic matter effects are often non-linear and non-consistent between different sediments (Koiter et al., 2013; Laceby et al., 2017; Koiter et al., 2019).

Stepwise discriminant analysis is then used to identify and weight the optimal group of tracers that best differentiate between different source groups while minimizing within-group tracer variability, done by selecting the tracers that minimize the computed value of Wilk's lambda (Collins et al., 1997). The developed sediments were highly variable in nature and although Sed\_SAT was able to classify them as a separate source, the tracers and transformations selected to do so reduced the ability of Sed\_SAT to properly classify and identify other sources. Furthermore, fingerprinting results including the developed sediments suggested that they were not a significant contributor to sediment unmixing models. Thus, we chose not to include developed sediments as a source in our results.

After removing developed sediments from the list of potential sources,  $\delta^{15}\text{N}$ , M3-Ca, Pb, M3-Si, Zn, and  $\delta^{13}\text{C}$  were the primary tracers identified as capable of differentiating between agricultural, forested, and stream bank sediments. Sed\_SAT

then uses the unmixing model in Equations (1) and (2) from Gellis and Gorman Sanisaca (2018) to apportion the target sediment into its constituent sources:

$$RE = \sum_{i=1}^n \left\{ \left( C_i - \left( \sum_{s=1}^m P_s S_{si} \right) \right) / C_i \right\}^2 W_i \quad (1)$$

$$\text{and} \\ \sum_{s=1}^n P_s = 1 \quad (2)$$

where RE is relative error;  $C_i$  is concentration of tracer (i);  $P_s$  is the optimized percentage of contribution of source type (s),  $S_{si}$  is the mean concentration of tracer i in source s;  $W_i$  is the weighting factor for each tracer i identified through discriminant analysis; n is the number of tracers; and m is the number of sediment source types;  $P_s$  is solved for through the minimization of RE.

A n=1000 Monte-Carlo simulation was then conducted with each run excluding one random source sample to evaluate model sensitivity. Further error analysis was conducted through a source verification test (SVT) where each source sample is ran through Sed\_SAT as if it were a target sample, with that source sample being removed from the list of potential sources. This procedure verifies both if the identified tracers can classify each source sample as well as the accuracy of the user selected source classification. A detailed explanation of Sed\_SAT and its procedures can be found in Gorman Sanisaca et al. (2017).

Sed\_SAT unmixing model accuracy were further evaluated through the fingerprinting of six known mixtures. Each mixture was created with one agricultural, forested, and storm sample each in known proportions and homogenized. Mixtures

four through six were further rewetted for four hours before re-drying and disaggregation.

As neither the storm suspended nor stream bed sediment unmixing models were significantly different ( $p > 0.05$ ) between the upstream and downstream sites on the Big Elk Creek, we chose to average the unmixing results from the two sites and present the data as a single Big Elk Creek sample. Storm suspended and stream bed sediment unmixing models are first presented as estimated proportions out of 100% for the 79 ha tributary and the Big Elk Creek. Sediment mass and nutrient yields were then determined at the upstream site using the averaged unmixing model results and the turbidity-SSC relationship.

### **3.8 Determination of sediment and nutrient exports and statistical analyses**

Suspended sediment yields were calculated for the study period with Equation 3:

$$Y_t = \int_0^t Q C_{est} dt \quad (3)$$

where  $Y_t$  is the total suspended sediment yield,  $Q$  is the instantaneous streamflow from the USGS gage,  $C_{est}$  is SSC estimated from the turbidity to SSC relationship at the upstream site, and  $t$  is time;  $Q$  was scaled by the ratio of the watershed areas at the USGS gaging station and the upstream field site. Discharge data were binned from 15-minute intervals to half hour intervals to match turbidity measurement frequency, and further offset by an hour to account for travel time between the location of our sonde and the USGS gaging station. Sediment yields for each event were calculated as the total sediment yield from the beginning to the end of each event, with the beginning time demarcated by the onset of precipitation and the

end time demarcated by either a return to baseflow conditions or the beginning of another event. While suspended sediment likely contained some coarse fractions (> 63 micron), we expect that much of the sediments were in the finer class.

Nutrient yields for storm events were determined through the mean nutrient concentration of each sediment source, the percent contribution of each source to each storm (derived from Sed\_SAT), and the total sediment yield of each storm to approximate nutrient yields from each sediment source (Equation 4).

$$Nut_{i,j} = \sum_{k=1}^z \bar{X}_{j,k} P_{i,k} Y_{i,j} \quad (4)$$

where  $Nut_{i,j}$  is the nutrient yield for nutrient  $j$  for event  $i$ ,  $\bar{x}_{j,k}$  is the mean concentration of nutrient  $j$  in source  $k$ ,  $P_{i,k}$  is the percent contribution of source  $k$  to event  $i$ , and  $Y_i$  is the total sediment yield for event  $i$ . We refer to this approach as the modeled nutrient yield. As the study watershed is a model verification site for the Phase 6 Chesapeake Bay Model (CBM), our modeled yields were then compared with both storm derived nutrient yields obtained through storm sediment yields and nutrient concentrations as well as Phase 6 CBM outputs for the Big Elk Creek.

Due to the non-normal distribution of much of our data, all evaluations of the significance of differences were determined through Wilcoxon rank-sum testing.

## Chapter 4

### RESULTS

#### 4.1 Source sediment and known mixture characterization

A linear discriminant analysis of the source data with the six most frequently identified tracers ( $\delta^{15}\text{N}$ , M3-Ca, Pb, M3-Si, Zn, and  $\delta^{13}\text{C}$ ) displays separation between the three source groups used in the unmixing models (Figure 4.1). Sediment unmixing model error analysis results are presented in Table 4.1. Forest and stream bank samples were the best-defined source groups, with  $90 \pm 15\%$  and  $88 \pm 17\%$  of samples correctly classified, respectively. Agricultural samples, however, were highly variable and the least well-identified ( $67 \pm 29\%$ ) source group, with 21% of agricultural samples falsely identified as bank samples and 10% as forest samples.

Table 4.1: Source verification test (SVT) results from individually running source samples through the unmixing model as target samples.

<b>Correct source type</b>		<b>Forest (%)</b>	<b>Agriculture (%)</b>	<b>Banks (%)</b>
<b>Forest</b> (n = 357)	Mean	90	1	9
	StDev	15	2	14
<b>Agriculture</b> (n = 561)	Mean	10	67	21
	StDev	13	29	21
<b>Banks</b> (n = 1173)	Mean	10	2	88
	StDev	17	6	17

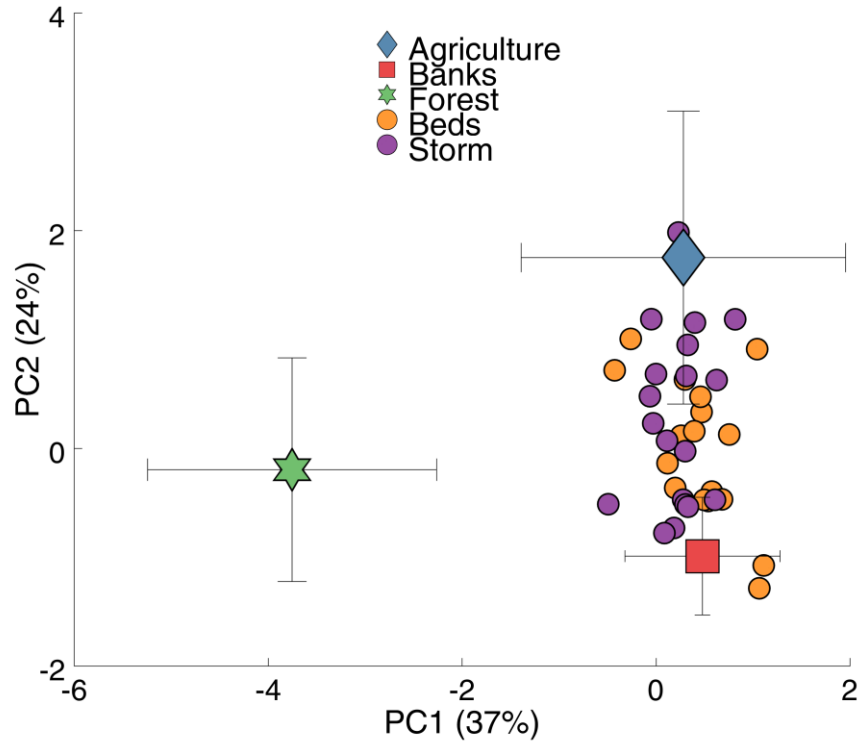


Figure 4.1: Principal component analysis of source and target data using the six tracers that were used in Sed\_SAT and included  $\delta^{15}\text{N}$ , M3-Ca, Pb, M3-Si, Zn, and  $\delta^{13}\text{C}$ . The plot shows clear separation between the sources and further than the storm and bed samples fall between the agricultural and stream bank sources.

Unmixing results of the known mixtures are presented in Table 4.2. In general, Sed\_SAT correctly identified the dominant constituent source to within 5% of the actual composition but misidentified the lesser constituent sources. The tracers identified by Sed\_SAT and used to unmix these models were the same as for the storm and bed target samples, but the results indicate that Sed\_SAT may not be ideal for identifying smaller source sediment contributions.

Table 4.2: Unmixing model results of the six known mixtures versus their actual composition. Mixtures M4 through M6 were rewetted, re-dried, and disaggregated again before analysis. All mixtures were made from the same source sediment samples, one each from the bank, agricultural, and forested source groups.

	Known			Modeled		
	Bank	Agr.	For.	Bank	Agr.	For.
<b>M1</b>	50	25	25	50	14	35
<b>M2</b>	25	50	25	15	47	38
<b>M3</b>	25	25	50	32	17	51
<b>M4</b>	50	25	25	45	23	32
<b>M5</b>	25	50	25	4	54	42
<b>M6</b>	25	25	50	20	30	50

#### 4.2 Storm events: hydrologic conditions, sediment and nutrient yields

A total of 10 storms were sampled over the study period (Table 4.3): four during Winter (Dec - Feb), three during Spring (Mar - May), two in Summer (Jun - Aug), and one in the Fall (Oct - Nov). All precipitation during these 10 events occurred as rainfall, with the largest amount of rainfall recorded during the July 23 (199 mm), May 17 (92 mm), and October 30 (65 mm) events (Figure 4.2). Antecedent precipitation varied with events: the February 11 (52 mm) and May 17 (61 mm) events had the highest total rainfall in the seven days prior, whereas the January 11 (1.8 mm) and April 16 (1.1 mm) had almost no rainfall prior to the event. Events with higher amounts of antecedent precipitation generally had higher peak discharges: the July 23 ( $170 \text{ m}^3 \text{ s}^{-1}$ ), May 17 ( $52 \text{ m}^3 \text{ s}^{-1}$ ), and May 14 ( $37 \text{ m}^3 \text{ s}^{-1}$ ) events were the largest events by peak discharge. The July 23, 2018 event had a recurrence interval of seven years and was the only sampled event with a recurrence interval greater than one year.

Table 4.3: Hydrologic conditions and sediment yields for the ten sampled storm events. Sediment yield is for the 114 km<sup>2</sup> Big Elk Creek sampling location.

Event Date	Total precip. (mm)	Rainfall duration (hr)	Event duration (hr)	Total discharge (mm)	Peak discharge (m <sup>3</sup> s <sup>-1</sup> )	API7 (mm)*	Sediment yield (kg ha <sup>-1</sup> )
30-Oct-17	64.7	22	72	8.1	18	10.7	5.08
11-Jan-18	32.3	21	63.5	7.4	14	1.8	12.45
5-Feb-18	27.4	11	65.5	6.0	17	7.8	23.97
8-Feb-18	20.1	9	78.5	6.6	17	33.3	26.76
11-Feb-18	40.1	25	107	15.4	31	52.1	49.15
16-Apr-18	32.3	22	139	9.7	17	1.1	5.00
14-May-18	37.6	19	73.5	11.7	37	11.7	95.15
17-May-18	91.7	65	158	35.3	52	61	320.00
11-Jun-18	25.80	11	43.5	4.5	15	9.6	**
23-Jul-18	199.2	56	207.5	66.8	170	28.6	714.61

\*API7 is the antecedent precipitation index, cumulative rainfall for seven days prior to the event.

\*\* not available

Suspended sediment yield at the upstream Big Elk Creek site was 1438 kg ha<sup>-1</sup> yr<sup>-1</sup> for the study period (Aug 1, 2017 – Jul 31, 2018; from Equation 3), with almost half of the sediment yield occurring during the large July 23, 2018 event. The May 17, 2018 event had the second highest suspended sediment yield at 320 kg ha<sup>-1</sup> yr<sup>-1</sup>, commensurate with its total precipitation and peak discharge rankings. The October 30, 2017 event, however, had lower sediment yields than all the succeeding Winter events, despite higher total precipitation and rainfall intensity than all the Winter events and higher peak discharge than three out of the four Winter events (Table 4.3).

Storm sediment nutrient concentrations tended to decrease with increasing discharge, though only P was significantly correlated with discharge (C: p = 0.11; N: p = 0.16; P: p < 0.01). The January 11, 2018 and April 16, 2018 events were notable despite their relatively low peak discharge and SSC yields: both events had little

antecedent rainfall in the seven days prior and occurred after two months of little rainfall. These events further had the highest nutrient concentrations of the sampled events: C (44710 mg kg<sup>-1</sup>) and P (1147 mg kg<sup>-1</sup>) concentrations were highest during the January 11, 2018 events, and N was highest during the April 16, 2018 event (4535 mg kg<sup>-1</sup>). Nutrient concentrations then decreased after these events in consecutive events, particularly during the three February and two May events that occurred in rapid succession. This depletion effect was most pronounced in C and N concentrations, and the events with the highest peak discharges generally had the lowest nutrient concentrations; the July 23 event had the lowest nutrient concentrations overall.

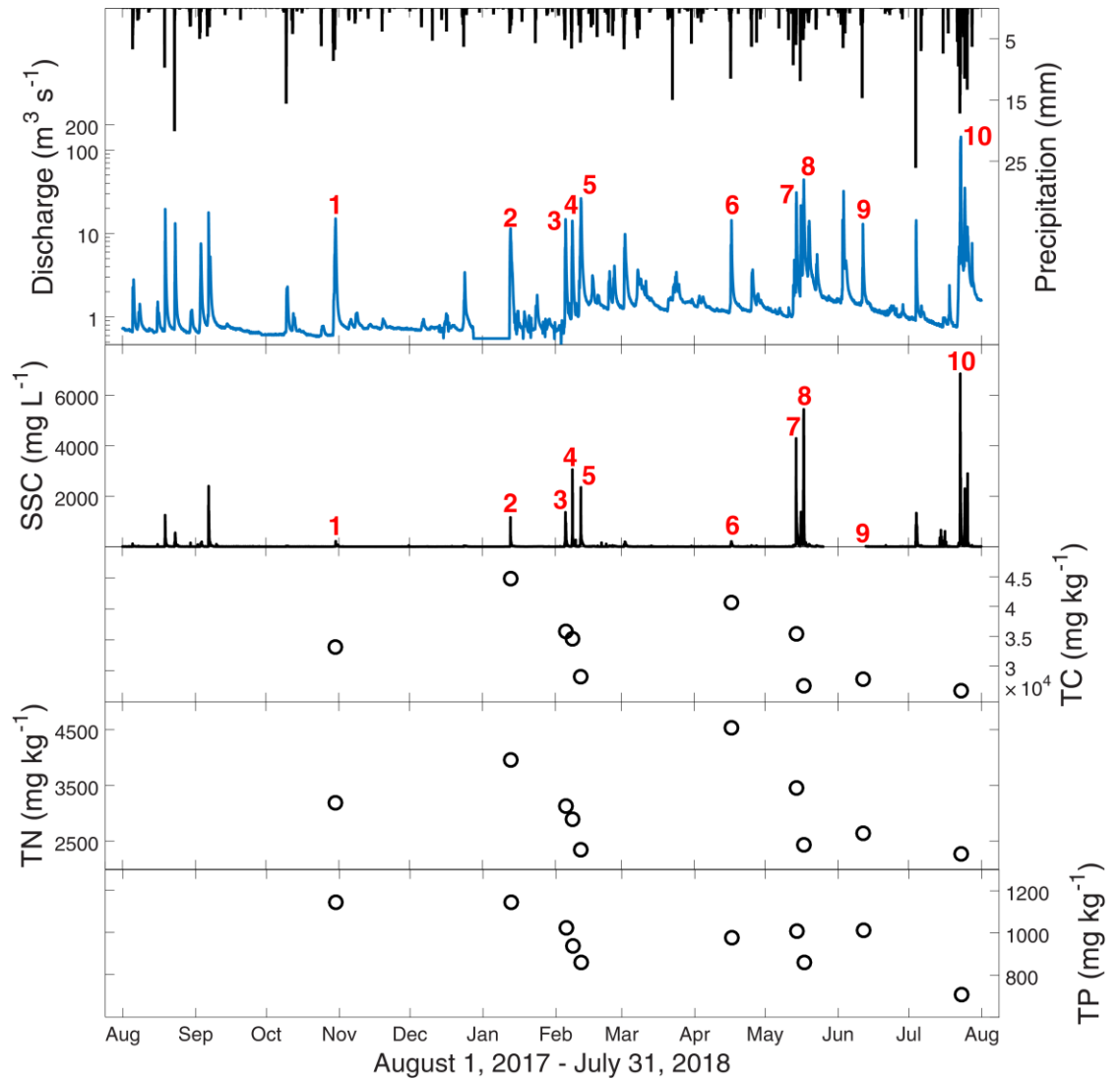


Figure 4.2: Time-series plot for the study period (August 1, 2017 – July 31, 2018) for precipitation (mm) and discharge ( $\text{m}^3 \text{s}^{-1}$ ); suspended sediment concentrations ( $\text{mg L}^{-1}$ ); and storm sediment C, N, and P concentrations ( $\text{mg kg}^{-1}$ ). The 10 sampled events are indicated in red for the hydrograph and SSC-time series. Discharge is plotted on a logarithmic scale and SSC data were not available for the sampled June 11, 2018 event due to instrumentation issues.

### **4.3 Erosion pin measurements**

Erosion pin measurements (changes in exposed pin length since installation) averaged for the two sites are presented in Figure 4.3. Positive values indicate degradation/erosion and negative values indicate sediment aggradation/deposition on the bank. The pins recorded two major periods of bank erosion: the first on February 15, 2018 when the pins recorded an average erosion of 5 cm from the date of installation. The pins recorded little-to-no erosion between installation in August 2017 and the February 2018 events; some deposition was recorded in January 2018. The pins were not measured between February and May 2018 as no major storm events occurred and bank conditions were observed to be static during weekly field excursions. Some deposition was recorded following the two May 2018 events. The second period of major erosion occurred during/following the July 23 event, where the erosion pins recorded an average of 10 cm of erosion. Visual observations of stream banks following this event confirmed that a substantial amount of bank erosion had occurred in the study reaches.

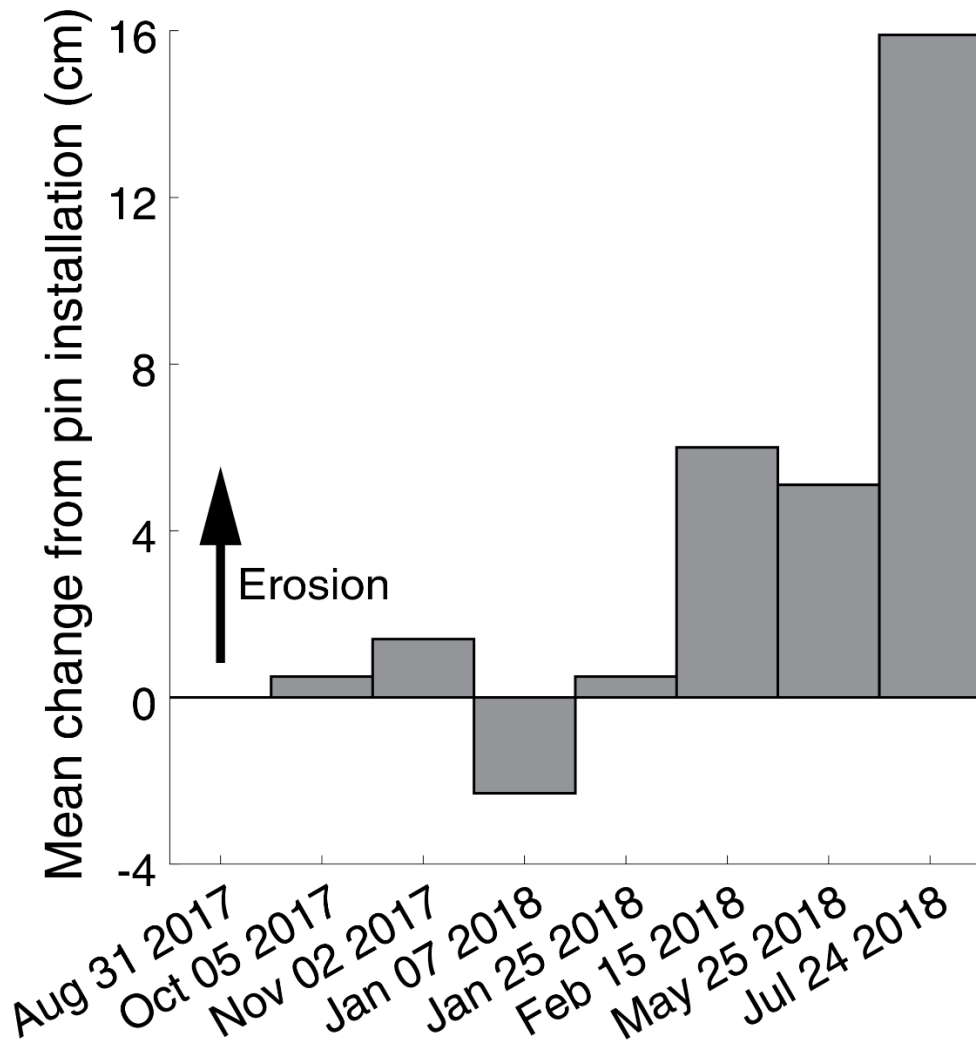


Figure 4.3: Erosion pin measurements presented in change in length of pin exposed during the date of measurement relative to pin length at installation (cm). Pins were installed on Aug 3, 2017. Net erosion at the end of the monitoring period was 15.9 cm of erosion, averaged over the two sets of erosion pins.

#### **4.4 Bed sediment composition**

Agricultural and stream bank sources comprised a majority of fine fractions of the stream bed sediments from both the 79 ha tributary and the Big Elk Creek (Figure 4.4). Wilcoxon rank sum tests revealed that stream bank contributions to stream bed sediments were not significantly different ( $p = 0.37$ ) between the Big Elk Creek ( $57 \pm 9\%$ ) and the 79 ha tributary ( $52 \pm 18\%$ ). There were no contributions attributed to forested soils at the predominantly forested 79 ha tributary, and only minor contributions from forested soils to the Big Elk Creek during November 2017 and November 2018. Stream bank contributions to bed sediments at the 79 ha tributary remained consistently near the mean of 52% during March to July of 2018. Stream bank contributions were more variable in the Fall of 2018: highest during September of 2018, lowest during October of 2018, then to 50% in November of 2018.

Stream bank contributions to bed sediments at the Big Elk Creek displayed a more pronounced temporal pattern than that for the 79 ha tributary. Stream bank contributions were significantly greater ( $p = 0.02$ ) during the Winter to Spring months ( $67 \pm 4\%$ ) compared to the rest of the year ( $51 \pm 11\%$ ). There was a precipitous decline in stream bank contributions during the Summer 2018, and stream bank contributions followed the same pattern of high in September, low in October, and high again in November as the 79 ha tributary, albeit with less extreme differences between months.

#### **4.5 Source contributions to storm suspended sediments**

Agricultural and stream bank sediments were the major contributors to storm suspended sediments with only minor contributions from forested soils (Figure 4.5). Considering all 10 storms,  $49 \pm 9\%$  of the fine suspended sediments were attributed to

stream banks for the 79 ha tributary, compared to  $42 \pm 9\%$  at the 114 km<sup>2</sup> Big Elk Creek location.

Stream bank contributions to the 79 ha tributary were highest during the May 17 event (66%), and were below 50% for the other six events. Forested soils were not found to contribute to suspended sediments at the 79 ha tributary. For the Big Elk Creek, the highest stream bank contributions occurred during the February 11 (50%), May 17 (53%), and July 23 (51%) events. Stream bank contributions were lowest during the June 11 (24%) and February 8 events (32%). Minor contributions from forested soils were found during the May 14 and May 17 events.

Total suspended sediment yield from forested, agricultural, and stream bank sediments for the nine events (yield data was not available for June 11 event) at the Big Elk Creek with suspended sediment yields are 4.8 kg ha<sup>-1</sup>, 618.5 kg ha<sup>-1</sup>, and 628.9 kg ha<sup>-1</sup>, respectively (Figure 4.6). A comparison of Figure 4.5 and Figure 4.6 indicates that stream banks contribute more to storm suspended sediments at the Big Elk Creek by mass than by percentage: stream banks account for 50% of the sediment yield by mass for the nine events with yield estimates, whereas stream banks account for 44% of the sediment yields by percent for the same nine events (42% including the June 11 event). This disparity is largely due to high yields for the May 17 and July 23 events.

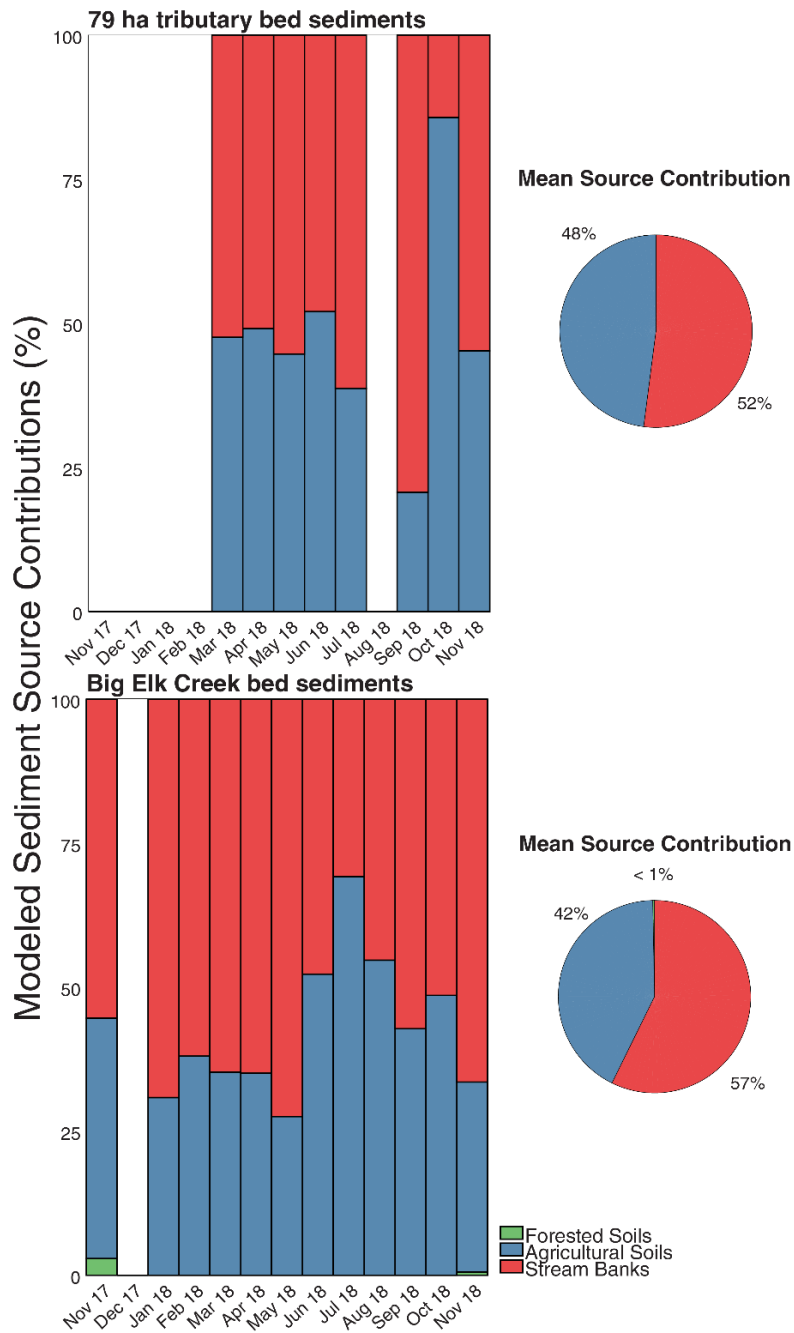


Figure 4.4: Source contributions by percent to fine stream bed sediments. Samples are labeled by the month and year during which they were collected. The pie charts display mean percent contributions by source to the unmixing models. Red is stream banks, blue is agricultural sediments, and green is forested soils.

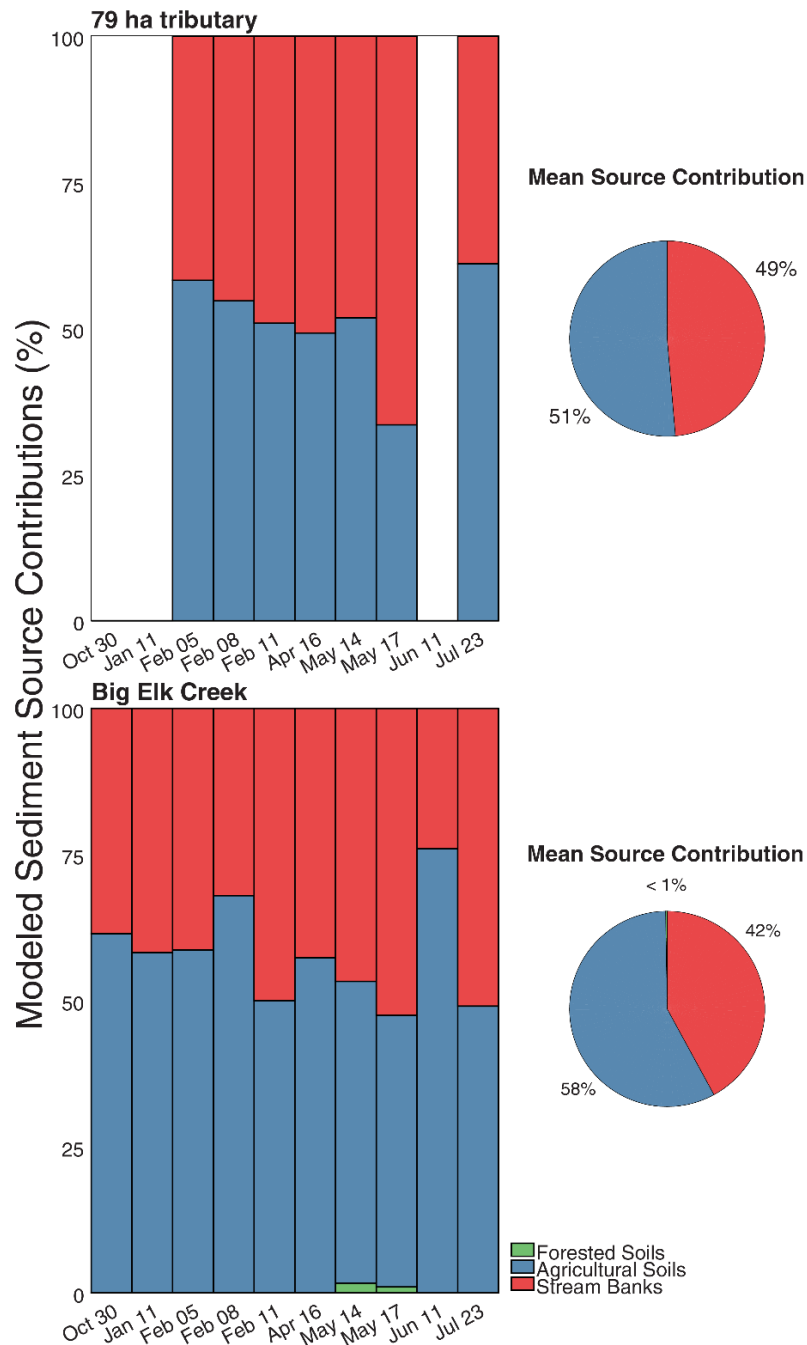


Figure 4.5: Source contributions by percent to fine suspended sediments from ten storm events, 2017 - 2018. Samples are labeled by the month and date of peak discharge of each event. The pie charts display mean percent contributions by source to the unmixing models. Red is stream banks, blue is agricultural sediments, and green is forested soils.

Both stream bank and agricultural sediment yields were significantly positively correlated with peak discharge (Figure 4.7A). Although stream bank (Figure 4.7B) and agricultural sediments (Figure 4.7C) by percent contribution exhibited a positive and a negative relationship with peak discharge, respectively, neither were significantly correlated. In general, stream bank and agricultural contributions do not exhibit a strong relationship with peak discharge. Events with a peak discharge over  $25 \text{ m}^3 \text{ s}^{-1}$ , however, had significantly higher stream bank contributions ( $p < 0.01$ ) and significantly lower agricultural contributions ( $p < 0.01$ ), by percent than events with a peak discharge below  $25 \text{ m}^3 \text{ s}^{-1}$ .

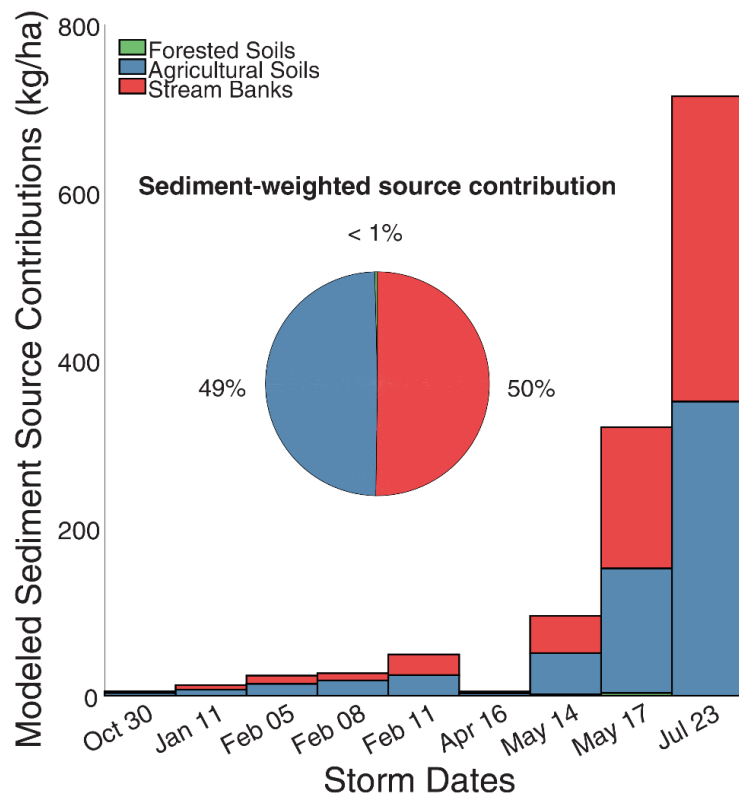


Figure 4.6: Sediment yield weighted source contributions in  $\text{kg ha}^{-1}$ . Samples are labeled by the month and date of peak discharge of each event. The pie chart displays total contributions from each source, by mass. Red is stream banks, blue is agricultural sediments, and green is forested soils.

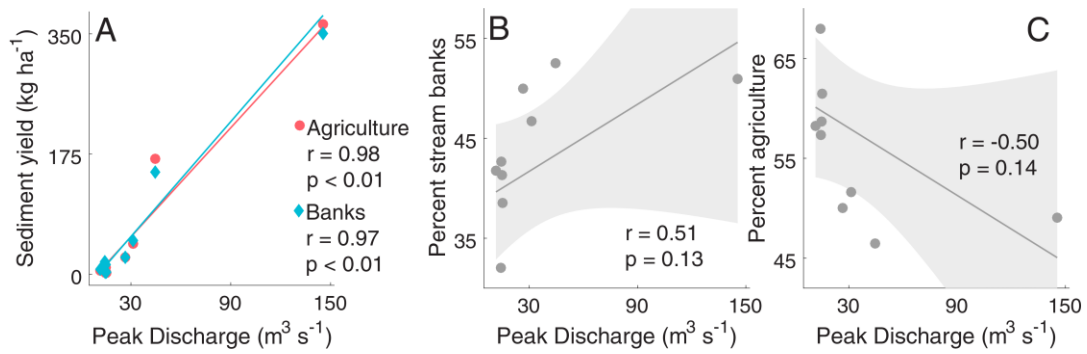


Figure 4.7: Relationships between peak discharge ( $\text{m}^3 \text{s}^{-1}$ ) and stream bank/agricultural contributions to storm yields by mass (A); stream bank contributions to storm unmixing models by percent (B); and agricultural contributions to storm unmixing models by percent (C).

#### 4.6 Source and target sediment nutrient concentrations

Stream bank nutrient concentrations were consistently lower than forested and agricultural soils (Table 4.4). Mean sediment-bound C and N were highest and most variable in the forested soils ( $11.5 \times 10^4 \pm 5.0 \times 10^4 \text{ mg kg}^{-1}$  and  $6017 \pm 2173 \text{ mg kg}^{-1}$ , respectively) while agricultural soils had the mean highest P ( $1162 \pm 305 \text{ mg kg}^{-1}$ ) and M3-P ( $108 \pm 89 \text{ mg kg}^{-1}$ ) concentrations; agricultural M3-P concentrations were highly variable between sites. Stream bed and storm suspended nutrient concentrations fall between upland nutrient concentrations, concomitant with sediment fingerprinting results. Stream bed sediment C, N, and P concentrations were significantly lower ( $p \leq 0.0434$ ) than those of storm suspended sediments. Soil organic N was the dominant form of N in all source samples ( $99 \pm .5\%$ ); forested soils had the highest  $\text{NH}_4\text{-N}$  concentrations ( $18.4 \pm 5.2 \text{ mg kg}^{-1}$ ) and agricultural soils had the highest  $\text{NO}_3\text{-N}$  ( $15.2 \pm 21.0 \text{ mg kg}^{-1}$ ) concentrations. Stream beds had higher  $\text{NH}_4\text{-N}$  ( $11.9 \pm 8.6 \text{ mg kg}^{-1}$ ) concentrations than its constituent agricultural ( $5.2 \pm 3.9 \text{ mg kg}^{-1}$ ) and stream bank ( $2.0 \pm 1.3 \text{ mg kg}^{-1}$ ) sediments.

Mean storm suspended total C concentrations were higher at the 79 ha tributary than at the Big Elk Creek ( $3.9 \times 10^4$  mg kg<sup>-1</sup> versus  $3.3 \times 10^4$  mg kg<sup>-1</sup>), whereas nitrogen (3086 mg kg<sup>-1</sup>) and P (968 mg kg<sup>-1</sup>) concentrations were higher at the Big Elk Creek than at the 79 ha tributary (2809 mg kg<sup>-1</sup> N, 727 mg kg<sup>-1</sup> P). Carbon and nitrogen concentrations were not significantly different ( $p = 0.06$ , C;  $p = 0.69$ , N) between the sites; total phosphorus and M3-P concentrations were higher ( $p < 0.01$ , P;  $p < 0.01$ , M3-P) for the Big Elk Creek than the 79 ha tributary.

Storm suspended sediment-bound nitrogen primarily comprised soil organic N at both sites. The 79 ha tributary, however, had significantly higher mean NH<sub>4</sub>-N ( $10.8 \pm 4.2$  mg kg<sup>-1</sup>) concentrations than the agricultural ( $5.2 \pm 3.9$  mg kg<sup>-1</sup>,  $p = 0.02$ ) and stream bank sediments ( $2.0 \pm 1.3$  mg kg<sup>-1</sup>,  $p < 0.01$ ); all but the February 08, 2018 event had NH<sub>4</sub>-N concentrations higher than the constituent stream bank and agricultural sediment sources in the proportions identified through fingerprinting. NH<sub>4</sub>-N concentrations for the Big Elk Creek ( $6.2 \pm 3.9$  mg kg<sup>-1</sup>) were lower than for the 79 ha tributary, but still higher than the constituent source concentrations. At the Big Elk Creek, this disparity mirrors an increase in NH<sub>4</sub>-N concentrations following the April 16 event (Table 4.4): the Fall 2017 event and three of the four Winter 2018 events had low NH<sub>4</sub>-N concentrations; the January 11, 2018 event was the exception.

Table 4.4: Mean nutrient concentrations for the sources and storm suspended sediments. Concentrations are presented as mean (one standard deviation).

<b>Sources</b>	<b>TC (mg kg<sup>-1</sup>)</b>	<b>TN (mg kg<sup>-1</sup>)</b>	<b>TP (mg kg<sup>-1</sup>)</b>	<b>NO<sub>3</sub>-N (mg kg<sup>-1</sup>)</b>	<b>NH<sub>4</sub>-N (mg kg<sup>-1</sup>)</b>	<b>Org N (mg kg<sup>-1</sup>)</b>	<b>M3-P (mg kg<sup>-1</sup>)</b>
Agriculture	34629 (12364)	3247 (1332)	1162 (305)	15.2 (21.0)	5.2 (3.9)	3226 (1332)	108.1 (89.0)
Forest	115030 (50821)	6017 (2173)	850 (286)	5.6 (4.9)	18.4 (5.2)	5993 (2165)	15.4 (6.9)
Stream banks	16070 (13404)	1167 (731)	550 (151)	9.8 (6.7)	2.0 (1.3)	1161 (731)	9.9 (6.6)
Stream beds	20571 (6542)	1718 (549)	661 (126)	4.9 (2.1)	11.9 (8.6)	1655 (521)	25.0 (6.2)
<b>79-ha storms</b>	<b>TC (mg kg<sup>-1</sup>)</b>	<b>TN (mg kg<sup>-1</sup>)</b>	<b>TP (mg kg<sup>-1</sup>)</b>	<b>NO<sub>3</sub>-N (mg kg<sup>-1</sup>)</b>	<b>NH<sub>4</sub>-N (mg kg<sup>-1</sup>)</b>	<b>Org N (mg kg<sup>-1</sup>)</b>	<b>M3-P (mg kg<sup>-1</sup>)</b>
5-Feb-18	36070	2550	688	3.7	18.2	2535	18.5
8-Feb-18	41740	2910	782	4.6	4.9	2910	15.8
11-Feb-18	34890	2440	673	1.8	9.7	2432	19.5
16-Apr-18	44890	3280	760	3.2	9.2	3274	17.0
14-May-18	42620	2970	791	1.7	13.9	2958	18.6
17-May-18	31260	2320	665	1.6	9.3	2312	23.8
23-Jul-18	40700	3190	728	4.1	10.5	3184	20.1
Mean	38881 (4890)	2809 (375)	727 (53)	3.0 (1.2)	10.8 (4.2)	2801 (377)	19.0 (2.5)
<b>Big Elk storms</b>	<b>TC (mg kg<sup>-1</sup>)</b>	<b>TN (mg kg<sup>-1</sup>)</b>	<b>TP (mg kg<sup>-1</sup>)</b>	<b>NO<sub>3</sub>-N (mg kg<sup>-1</sup>)</b>	<b>NH<sub>4</sub>-N (mg kg<sup>-1</sup>)</b>	<b>Org N (mg kg<sup>-1</sup>)</b>	<b>M3-P (mg kg<sup>-1</sup>)</b>
30-Oct-17	33130	3185	1144	19.9	2.4	3163	35.2
11-Jan-18	44710	3960	1147	4.6	8.3	3947	34.8
5-Feb-18	35800	3130	1026	2.8	3.1	3124	34.4
8-Feb-18	34615	2895	938	27.0	4.2	2864	36.4
11-Feb-18	28275	2345	859	3.2	1.5	2340	36.2
16-Apr-18	40680	4535	978	1.3	9.5	4524	19.0
14-May-18	35420	3455	1010	3.4	9.0	3443	34.6
17-May-18	26685	2440	861	5.2	10.4	2424	38.2
11-Jun-18	27850	2640	1013	5.8	11.5	2623	43.0
23-Jul-18	25930	2270	709	7.2	2.2	2261	31.4
Mean	33310 (6237)	3086 (736)	968 (135)	8.0 (8.5)	6.2 (3.9)	3071 (736)	34.3 (6.2)

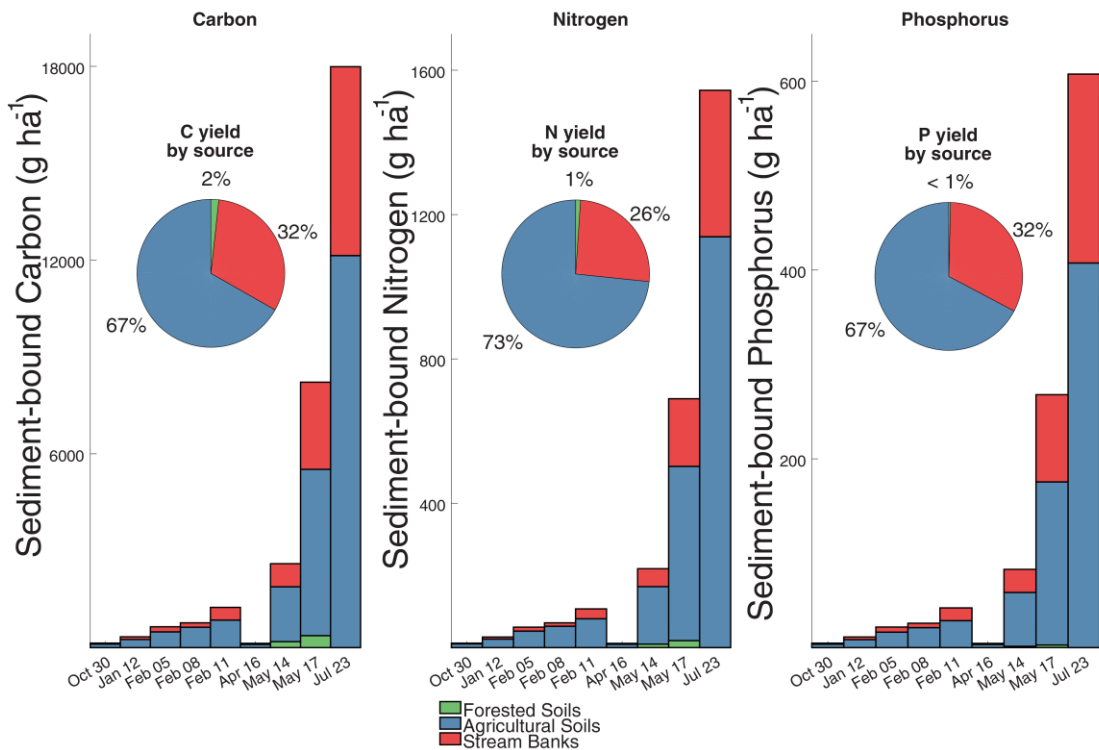


Figure 4.8: Storm sediment nutrient (C, N, P) yields in  $\text{g ha}^{-1}$  calculated from Equation 4. Samples are labeled by the month and date of peak discharge of each event. The pie chart displays total nutrient contributions from each source, by mass. Red is stream banks, blue is agricultural sediments, and green is forested soils.

Nutrient yields from Equation 4 from the Big Elk Creek are presented in Figure 4.8. Nutrient yields were dominated by contributions from the high discharge events: 92% of the total C, N, and P yields from the nine events occurred during the four events with a peak discharge over  $25 \text{ m}^3 \text{ s}^{-1}$  (February 11, May 14, May 17, July 23). As stream bank sediments had lower sediment concentrations than the upland source sediments, they contributed less by mass to watershed nutrient yields than to watershed sediment yields. Overall, we find that 32% of sediment-bound C, 26% of

sediment-bound N, and 32% of sediment-bound P were attributed to stream bank sources (Figure 4.8).

Our modeled nutrient yields generally underpredicted nutrient yields derived from storm sediment nutrient concentrations (Table 4.5). January 11 and April 16, the two events with the highest storm sediment nutrient concentrations, generally had the lowest convergence between modeled and storm-derived nutrient yields. The modeled nutrient yields tended to converge with the storm-derived yields during the events with higher peak discharges, and consequentially the events with higher stream bank contributions. No significant relationships were found, however, between percent stream bank contributions or peak discharge with nutrient yield comparisons. Overall, P yields matched up better (94% between modeled/storm-derived) than the C and N yields (81% and 77%, respectively), and in some cases the modeled P yields exceeded the storm-derived yields: the modeled yield for the July 23 event was 120% that of the storm-derived yield.

Table 4.5: Comparison of source derived versus storm derived nutrient yields for the sampled events; the ratio is expressed as source yield divided by storm yield.

<b>Carbon</b>						
<b>Storm date</b>	<b>Agr. yield (g/ha)</b>	<b>For. yield (g/ha)</b>	<b>Bank yield (g/ha)</b>	<b>Source yield (g/ha)</b>	<b>Storm yield (g/ha)</b>	<b>Ratio</b>
<b>10/30/2017</b>	108.2	0.0	31.5	139.7	168.4	83%
<b>1/12/2018</b>	251.0	0	83.5	334.6	556.5	60%
<b>2/5/2018</b>	487.1	0	159.2	646.2	858.1	75%
<b>2/8/2018</b>	629.8	0	137.8	767.6	926.3	83%
<b>2/11/2018</b>	851.5	0	394.8	1,246.3	1,389.8	90%
<b>4/16/2018</b>	99.3	0	34.3	133.6	203.4	66%
<b>5/14/2018</b>	1,700.8	182.8	714.3	2,597.9	3,370.4	77%
<b>5/17/2018</b>	5,149.6	370.0	2,700.8	8,220.3	8,539.3	96%
<b>7/23/2018</b>	12,139.3	0	5,850.4	17,989.8	18,529.9	97%
<b>Nitrogen</b>						
<b>Storm date</b>	<b>Agr. yield (g/ha)</b>	<b>For. yield (g/ha)</b>	<b>Bank yield (g/ha)</b>	<b>Source yield (g/ha)</b>	<b>Storm yield (g/ha)</b>	<b>Ratio</b>
<b>10/30/2017</b>	10.1	0.0	2.2	12.3	16.2	76%
<b>1/12/2018</b>	23.5	0	5.8	29.3	49.3	60%
<b>2/5/2018</b>	45.7	0	11.0	56.7	75.0	76%
<b>2/8/2018</b>	59.1	0	9.6	68.6	77.5	89%
<b>2/11/2018</b>	79.8	0	27.4	107.2	115.3	93%
<b>4/16/2018</b>	9.3	0	2.4	11.7	22.7	52%
<b>5/14/2018</b>	159.5	9.6	49.6	218.6	328.8	66%
<b>5/17/2018</b>	482.9	19.4	187.4	689.6	780.8	88%
<b>7/23/2018</b>	1,138.3	0	405.8	1,544.2	1,622.2	95%
<b>Phosphorus</b>						
<b>Storm date</b>	<b>Agr. yield (g/ha)</b>	<b>For. yield (g/ha)</b>	<b>Bank yield (g/ha)</b>	<b>Source yield (g/ha)</b>	<b>Storm yield (g/ha)</b>	<b>Ratio</b>
<b>10/30/2017</b>	3.6	0.0	1.1	4.7	5.8	81%
<b>1/12/2018</b>	8.4	0	2.9	11.3	14.3	79%
<b>2/5/2018</b>	16.3	0	5.4	21.8	24.6	89%
<b>2/8/2018</b>	21.1	0	4.7	25.9	25.1	103%
<b>2/11/2018</b>	28.6	0	13.5	42.1	42.2	100%
<b>4/16/2018</b>	3.3	0	1.2	4.5	4.9	92%
<b>5/14/2018</b>	57.1	1.4	24.4	82.9	96.1	86%
<b>5/17/2018</b>	172.8	2.7	92.4	268.0	275.5	97%
<b>7/23/2018</b>	407.4	0	200.2	607.6	506.7	120%

## Chapter 5

### DISCUSSION

#### 5.1 Sediment yields and source contributions

Annual sediment yield from the Big Elk Creek for the study period (August 1, 2017 to July 31, 2018) was greater than those reported for other Piedmont watersheds and physiographic regions of the Chesapeake Bay (Table 5.1). However, this was primarily due to the large, seven-year recurrence interval July 23 event which contributed 715 kg ha<sup>-1</sup> of suspended sediment. Sediment yield for the Big Elk Creek without the July 23, 2018 event would have been 633 kg ha<sup>-1</sup> yr<sup>-1</sup>, within the range of Coastal Plain and Piedmont watershed sediment yields reported by Gellis et al. (2005).

Table 5.1: Comparison of this study's sediment exports with other Chesapeake Bay watersheds in different physiographic provinces. Data adapted from Gellis et al., 2005.

<b>Physiographic region/Watershed</b>	<b>Annual sediment yield (kg ha<sup>-1</sup> yr<sup>-1</sup>)</b>
Appalachian Plateau	588
Blue Ridge	568
Valley & Ridge	663
Piedmont	1037
Coastal Plain	119
Big Elk Creek (Piedmont; this study)	1345

Fingerprinting results indicate that bank-derived sediment is a substantial, if not dominant contributor to suspended sediment yields in the Big Elk Creek. Our average SSC-weighted bank contribution value of 50% was within the range of values reported by other fingerprinting studies incorporating bank-derived sediment along the East Coast of the US (Table 5.2). Sediment contributions from forested soils were low

overall, concordant with findings from other fingerprinting studies (Gellis and Noe, 2013; Gellis et al., 2018, Cashman et al., 2018). Similar to Cashman et al. (2018), we attribute low-to-no forested contributions to the armoring of forested soils by dense canopy cover during Spring and Summer, and a thick layer of leaf litter during the Fall and Winter; during our source sampling, leaf litter had to be removed prior to forested soil collection at every location.

Similar to Gellis and Noe (2013), agricultural and stream bank sediments are the dominant sources of suspended sediment in the study watershed. Stream bank contributions to the Big Elk Creek were lower than those found by Cashman et al. (2018) at Upper Difficult Run, VA and Massoudieh et al. (2013) at Mill Stream, MD. Cashman et al. (2018) suggested that the erosion of legacy-impacted stream banks was likely exacerbated by the urban stream syndrome and “flashier” storm events: the urban stream syndrome results in higher and flashier peak flows (Walsh et al., 2005), which may have induced higher stream bank contributions from fluvial erosion. In Massoudieh et al. (2013), the channel was buffered by large forested areas which favored deposition of agricultural sediments transported by overland flow, resulting in higher contributions from near-channel sources. We did not find evidence of intense urbanization or the urban stream syndrome in the Big Elk Creek, and visual observations made during source sampling as well as NLCD data suggested that many croplands were not extensively buffered by forested areas (NLCD, 2011).

Stream bank and forest sediments were generally well constrained and classified in Sed\_SAT. The poorer classification of agricultural sediments may be due to our decision to combine croplands and pastures into a single agricultural sediment source. This decision was made because Sed\_SAT was not able to reliably

differentiate between pasture and cropland soils. These findings are similar to that of Gellis and Gorman Sanisaca (2018), who also reported poor source verification results on pastures, attributed to a lack of change in soil chemistry between current and legacy land uses.

Table 5.2: Comparison of stream bank contributions to storm suspended sediments from selected studies in the Mid-Atlantic region.

Study	Watershed	Dominant land-use	Geographic setting	Fingerprints	Sediment sources	Avg. bank contribution
This study	Big Elk Creek, MD (164 km <sup>2</sup> )	Agricultural	Mid-Atlantic Piedmont	$\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ , M3-elements, heavy metals	Banks, cropland, forest	50%
Gellis et al., 2009	Pocomoke River, MD (157 km <sup>2</sup> )	Agricultural	Mid-Atlantic Coastal Plain	Radionuclides, $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ , TC, TN	Banks, stream beds & ditches, cropland, forest	7%
Gellis et al., 2009	Mattawoman Creek, MD (134 km <sup>2</sup> )	Agricultural	Mid-Atlantic Coastal Plain	Stable isotopes ( $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ , TC, TN)	Banks, construction, cropland, forest	31%
Gellis et al., 2009	Little Conestoga Creek, PA (110 km <sup>2</sup> )	Agricultural/Urban	Mid-Atlantic Piedmont	Total phosphorus, stable isotopes ( $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ )	Banks, construction sites, cropland	23%
Mckinley et al., 2012; Mukundan et al., 2010	North Fork Broad River, GA (182 km <sup>2</sup> )	Forested	Southern Piedmont	TC, $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$	Banks, subsurface, pasture	68% - 80%
Voli et al., 2013	Four catchments within Falls Lake, NC watershed; total 150 km <sup>2</sup>	Urban to forested	Southern Piedmont	Heavy metals, rare earth elements, radionuclides	Banks, roads, construction, forest	62%, 58%, 33%, 27%
Massoudieh et al., 2013	Mill Stream Branch, MD (31.6 km <sup>2</sup> )	Agricultural	Mid-Atlantic Coastal Plain	Elemental metals	Stream corridor, croplands, forests	94%
Gellis & Noe, 2013	Linganore Creek, MD (147 km <sup>2</sup> )	Agricultural	Mid-Atlantic Piedmont	$\delta^{13}\text{C}$ , TC, TN, V, Cu, Li	Banks, cropland, forest	53%
Cashman et al., 2018	Upper Difficult Run, VA (14.2 km <sup>2</sup> )	Suburban	Mid-Atlantic Piedmont	Bulk metals, trace elements, stable isotopes ( $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ )	Banks, forest, roads	87%

## 5.2 Role of in-channel storage in suspended sediment yields

Previous research has suggested that the remobilization of stream bed sediments may be an important source of fluvial suspended sediment (Gellis et al., 2017; Cashman et al., 2018; Mahoney et al., 2018). Quantifying stream bed contributions to suspended sediment yields is complicated/difficult because stream beds or channel stores are a secondary source formed from the combination of primary sediment sources such as upland agricultural, forested, and stream bank sediments. Stream bed sediments may potentially be considered as a unique source if they acquire a chemical signature distinct from its constituent sources. Although Mahoney et al. (2018) identified that stream bed sediments accrued a unique, autotrophic (algal) signature in  $\delta^{13}\text{C}$  concentrations in a Midwestern watershed with negligible contributions from stream banks to suspended sediment yields, we were not able to make this distinction in this study.

In lieu of sediment fingerprinting, estimates of stream bed remobilization are typically made with fallout radioisotope tracers or mass balance approaches. Gellis et al. (2016) found that fine suspended sediment samples from 78 of 99 sampled Midwestern watersheds were dominated by (>50%) channel and bed-derived sediment; the remainder of the suspended sediment was attributed to surficial sediments <100 days old. These results are consistent with Cashman et al. (2018) found that direct stream bank erosion could not account for their observed bank-derived suspended sediment yield without factoring in erosion from stream beds and stream bars. We similarly speculate that the remobilization of stream bed sediments was an important source to watershed suspended sediment yields in the Big Elk Creek.

We found no significant correlations between peak discharge and sediment sources, consistent with the findings of Gellis and Gorman Sanisaca (2018). Our

results suggest that our storm events fell into two significantly different groups based on the event's peak discharge: sampled events with peak discharges over  $25 \text{ m}^3 \text{ s}^{-1}$  had significantly higher bank contributions and significantly lower agricultural contributions, by percent, than events with a peak discharge below  $25 \text{ m}^3 \text{ s}^{-1}$  (Figure 4.7B, 4.7C).

Peak discharge is an important factor in stream bank erosion, removing material eroded by freeze-thaw and mass wasting processes and causing fluvial bank erosion (Gellis and Noe, 2013). The significantly higher bank contributions during the sampled high peak discharge ( $>25 \text{ m}^3 \text{ s}^{-1}$ ) events may be attributed to stream bank material from direct fluvial erosion and suggests a threshold at which the critical shear stress required for fluvial bank erosion occurs: the February 11, 2018, May 14, May 17, 2018, and July 23, 2018 events all fall in this category. These four events were responsible for  $1178 \text{ kg ha}^{-1}$ , or 87% of the sediment yield by mass from the Big Elk Creek over the year-long study period. Of these events, only the July 23 event had a greater than one-year recurrence interval and was the only event during the study period to have exceeded the National Weather Service's flood stage designation. Stream bank contributions from these four events totaled  $601 \text{ kg ha}^{-1}$ , 45% of the annual sediment yield. Our erosion pin measurements (Figure 4.3) confirm that large amounts of bank erosion occurred following the three February 2018 and July 23, 2018 storm events. Little-to-no erosion was recorded following the two May 2018 events and may be attributed to the replacement of eroded stream bank sediments by storm deposited sediments.

### **5.3 Temporal variation in source contributions**

Stream bank contributions to both stream bed and storm suspended sediments were high during Winter 2018 and could be attributed to freeze-thaw bank erosion (Figure 4.3, Figure 4.4). The influence of freeze-thaw processes on stream bank erosion is well accepted (Wolman, 1959; Gatto, 1995). Couper (2003) further established that stream banks comprising fine silt/clay material, typical of banks with legacy sediments, are particularly susceptible to freeze-thaw processes. Freeze-thaw erosion was observed in the Big Elk Creek during the study period from late Fall 2017 to Winter 2018, culminating in the three successive February storm events. Bank erosion is also supported by the erosion pin measurements made after the February 11, 2018 event (Figure 4.3).

Stream bank contributions to wintertime bed and storm suspended unmixing models, however, were not significantly higher than other seasons at either the Big Elk Creek or the 79 ha tributary. This is attributed to bare ground conditions within the watershed as well as the timing of sampled high discharge events. Gellis et al. (2009) observed that bare ground conditions are common in agricultural areas post harvesting and before the growing season, and that disproportionately high sediment yields from agricultural lands could be attributed to bare ground conditions. During source sampling in Fall 2017 we observed that many crop fields upstream of the Big Elk Creek study sites were bare and often cultivated up to the edge of the stream banks, with no intermediate buffer zones or strips. These conditions may have allowed for enhanced erosion from agricultural fields during the Winter months, offsetting increased stream bank contributions from freeze-thaw erosion.

Barring high-intensity and high peak discharge Winter rainfall as observed in Inamdar et al. (2017) and Gellis and Noe (2013), agricultural and stream bank

sediments may deposit in the stream beds and serve as a supply of sediments for future storm events. Higher intensity and magnitude Spring and Summer rainfall then remobilize sediments from the stream bed. We observed a decrease in bank sediment contributions to stream beds after May 2018, attributed to a depletion of bank sediments in bed storage following the cessation of freeze-thaw processes in the Spring and thus a cessation in the supply of stream bank material to the stream beds. We did not sample an event in early June 2018 with a higher peak discharge than the sampled June 11, 2018 event. We hypothesize that this unsampled event depleted the last of the supply of stream bank material in stream bed sediments derived from Winter-time freeze-thaw erosion, thus explaining low stream bank contributions to both the June 11, 2018 and the Summer stream bed sediment unmixing models. The timing of bed sediment depletion may also explain why our erosion pins recorded net erosion following the July 23, 2018 event but not following the May 2018 events: the May 2018 events occurred before the depletion of bed sediment stores in June whereas the July event occurred after.

Temporal patterns in Fall stream bed compositions can also be explained by climactic factors. The Big Elk Creek received more than twice as much rainfall in September of 2018 than the 30-year (1981 – 2010) average for September (Maryland State Climatologist, accessed February 25, 2019). Bed sampling that month occurred between a series of three storms with a one-year recurrence interval, and increased bank sediment contributions likely reflect fluvially eroded bank sediment redeposited within the channel. In contrast, the watershed received an average amount of precipitation in October 2018 and bed sampling occurred after a minor rain event (<1 year recurrence) on October 27, 2018. This event, however, coincided with the most

active crop harvesting time in the agricultural lands upstream of our field sites. Low bank contributions and high agricultural contributions to bed sediments from October are likely a reflection of agricultural activity and may account for the agricultural contributions to the October 30, 2017 storm unmixing model.

An increase in bank contributions to stream beds in November 2018 can be explained by the onset of stream bank freeze-thaw erosion, corroborated by air temperature data from the adjacent weather station. November 2018 was the wettest November on record in the Mid-Atlantic region (NOAA, 2019), and a rain event occurred shortly before bed samples were collected. These factors would have resulted in substantial stream bank erosion during the month and consequentially redeposition of fine stream bank material in the stream beds.

#### **5.4 Nutrient loadings and sources**

Stream bank sediments had the lowest nutrient concentrations of our sampled sources (Table 4.3). Stream bank C and N concentrations were within the range of  $12.7 \times 10^3$  -  $15.0 \times 10^3$  mg kg<sup>-1</sup> C and 800 – 1700 mg kg<sup>-1</sup> N found in other studies (Gellis and Noe, 2013; McKinley et al., 2013; Weitzman et al., 2014). Less data are available for reactive N and P species, but studies have reported total P concentrations ranging from 340 – 958 mg kg<sup>-1</sup> (Walter and Merritts, 2008) and NO<sub>3</sub>-N and NH<sub>4</sub>-N concentrations of 4 mg kg<sup>-1</sup> and 3 mg kg<sup>-1</sup>, respectively (Weitzman et al., 2014). Elevated NO<sub>3</sub>-N concentrations in our stream banks may be indicative of nitrification in surficial bank sediments or nutrient inputs from groundwater (Weitzman et al., 2014; Spalding and Exner, 1993). Total P concentrations within our sampled stream banks are above the threshold of 250 mg kg<sup>-1</sup> proposed by Fox et al. (2016) at which sediments could potentially desorb P into the water column.

Agricultural and forested soils in this study had significantly higher nutrient concentrations than stream bank sediments, although  $\text{NH}_4\text{-N}$  comprised a smaller fraction of total forested N due to high total N concentrations and variability. High variability in forested C and N concentrations are attributed to our surficial sampling: some forested samples may have had more of the O horizon sampled than others. Both P and M3-P concentrations were low in forested soils but still higher than stream bank sediments.

Stream bed and storm suspended sediment nutrient concentrations both fall between source sediment nutrient concentrations. Stream bed nutrient concentrations are significantly lower than storm suspended sediment nutrient concentrations ( $p < 0.01$ ). These results are concordant with our sediment unmixing models, as the stream bed unmixing models had significantly higher low-nutrient stream bank contributions than the storm suspended samples by percent. Stream bed sediments, however, had higher  $\text{NH}_4\text{-N}$  concentrations than both agricultural and stream bank sediments, potentially due to sorption of  $\text{NH}_4\text{-N}$  from the water column, concordant with Triska et al. (1994).

A companion study found that stream bank nutrient concentrations were insignificantly temporally variant (Lutgen 2019), and thus the decrease in storm sediment C, N, and P concentrations with successive events (Figure 4.2) may be attributed to temporal variability in agricultural sediment nutrient concentrations. This is supported by Collins et al. (2019), who found significant decreases in agricultural sediment C and N concentrations within the span of two months. The increase in storm sediment nutrient concentrations during storms following long dry periods suggests a

“recharge” factor in upland nutrient concentrations, which may potentially be attributed to agricultural fertilizer additions.

As sediment yields are significantly correlated with peak discharge (Figure 4.7A), sediment-bound nutrient yields to the Big Elk Creek are highest during large storm events. While the largest storm events by peak discharge over our study period occurred primarily during the Spring and Summer months, historical data indicate that 59% (51/86) of the largest storms of each year occurred during the Winter and Spring months (Table 5.3). Large storms during the Winter and Spring months are of especial concern as that is when the supply of sediment and sediment-bound nutrients from freeze-thaw and bare-ground erosion is greatest. The historical data further indicate that 29% of the largest storms of each year occurred during the Summer months. Large summer events, such as the July 23 event sampled as a part of this study are especially problematic as their associated sediment and nutrient yields are exported into the bay during the most critical period for Bay habitats and ecosystems (Dennison et al., 2012).

Based on our sampled events, we find that stream banks contribute more to Chesapeake Bay nutrient yields (32%) than previously reported: Ibison et al. (1990) and Boynton et al. (1995) reported that stream bank erosion was a negligible source of N and only approximately 10% of P inputs to the Chesapeake Bay. Our findings are further similar to a study done in an agricultural Oklahoman watershed: Purvis et al. (2016) reported that stream bank erosion contributed approximately 31% of total P and 1% of dissolved P to watershed nutrient loads. Both our study and Purvis et al. (2016) were conducted in watershed with high eroding stream banks, and our results

suggest that stream bank erosion comprises a significant source of total P to watershed yields.

The discrepancies between our modeled and storm sediment-derived nutrient yields may be attributed to changes in source sediment nutrient concentrations, particularly in the agricultural soils. This is corroborated the divergence between modeled and source-derived nutrient yields during the April 16 event, coinciding with the timing of fertilizer application. Furthermore, the events with the highest storm sediment nutrient concentrations had relatively low rainfall intensity, duration, and peak discharges – higher nutrient concentrations during these events may not be as representative of storm sediment nutrient yields as the larger storms, which had better convergence between the modeled and source-derived nutrient yields.

## **5.5 Broader environmental and policy implications**

The goal of the Chesapeake Bay TMDL program is to accomplish 60% of Chesapeake Bay pollutant reduction targets by 2017, and 100% of the targets by 2025 (USEPA, 2018). As of 2018, it was reported that the 2017 targets had been met for phosphorus and sediment, but not for nitrogen. These reductions have largely been accomplished through pollutant load reduction from upland sources such as agriculture, stormwater, and wastewater treatment plants (USEPA, 2018). This is primarily because Chesapeake Bay BMPs have been designed and implemented under the Phase 5 Chesapeake Bay Watershed Model, which does not explicitly consider in-channel pollutant generation (USEPA, 2010; Chesapeake Bay Program, 2018). This oversight is not limited to just the Chesapeake Bay. A sediment TMDL developed for the Smith Creek in Virginia, for example, assigned 80% of suspended sediment yields to pasture sources (VADEQ, 2009). A sediment fingerprinting study conducted in the

watershed, however, found that only about 10% of suspended sediment yields could be attributed to pasture sources, with streambanks comprising the primary source (76%) of suspended sediment (Gellis and Gorman Sanisaca, 2018).

Stream banks and stream beds have been included in the Phase 6 Chesapeake Bay Program (CBP) Model, implemented in 2018 (Miller et al., 2019). The Big Elk Creek is a calibration site for the CBP Model, and thus we were able to compare our results with CBP model results: the CBP Model estimated an average sediment yield of  $1,739 \text{ kg ha}^{-1} \text{ yr}^{-1}$  over the calibration period of 1984 to 2014, slightly higher than our yield of  $1,348 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (Bhatt, 2019). Model calibration results further attribute 41% of sediment yields and 23% of total P yields to stream bank sources, comparable to our findings of 50% contribution to sediment yields and 32% contribution to P yields from stream bank sources (Bhatt, 2019).

The results of this study indicate that sediment and nutrient inputs from stream bank legacy sediments are not small and cannot be disregarded. This is particularly the case in the Mid-Atlantic where large stores of legacy sediment exist in the valley-bottoms of watersheds as a result of historic milling, associated impoundments, and legacy activities (Water and Merritts, 2008). By not explicitly accounting for legacy sediments and their inputs from stream banks and channel storage we may be getting an inaccurate picture of the sediment and nutrient loadings and importantly misallocating our BMP and restoration efforts for sediment and nutrient mitigation.

This disconnect has major implications for policymaking: a 2005 study estimated that approximately \$1 billion USD was spent each year on stream restoration projects annually (Hassett et al., 2005), and another study estimated that at least \$400 million USD had been spent on restoration projects within the Chesapeake

Bay watershed. If these TMDLs and restoration projects did not and do not consider the role of in-channel pollutant generation – stream banks in particular – then these funds have not been spent effectively. Our results reinforce the importance of stream banks in watershed sediment budgets and may help with model verification and testing, particularly as a recent Chesapeake Bay Program Scientific and Technical Advisory Committee report called for increased research on stream bank contributions to watershed nutrient budgets (Miller et al., 2019).

Further research into stream bank sediment and nutrient contributions to watershed exports must be performed given that dam removals have gained increased prominence and acceptance as a river management tool in the last few decades (e.g., Bellmore et al., 2017; Foley et al., 2017; Tullos et al., 2016). Dam removals and breaching can however make streambanks with legacy sediments more vulnerable to erosion and collapse (Merritts et al., 2011), increasing the sediment and nutrient loadings from these sources. While improvement in fish habitat has been the primary motivator for dam removals, we need to find out how dam removals may affect sediment budgets and their potential implications for water quality mitigation and watershed management.

Within a Mid-Atlantic Piedmont watershed, we found that stream bank sediment contributions by mass are significantly correlated with increasing discharge. These factors are compounded by freeze-thaw processes priming stream banks for erosion during the Winter and early Spring (Inamdar et al., 2017). Suspended sediment and nutrient yields from large events during the Winter and early Spring are especially problematic due to their impact on downstream aquatic life (Dennison et al., 2012).

Increased climate variability may result in the intensification of storm events (Melillo, 2014) and polar vortex instability (Zhang et al., 2016). These conditions may lead to an increase in freeze-thaw erosion cycles and an increase in the frequency of large rain events, and thus an increase in the supply and transport of sediments and sediment-bound nutrients, respectively (Inamdar et al., 2017). The impacts of increased climactic variability on stream bank erosion may be exacerbated by urbanization and the urban stream syndrome: “flashier” storm events may lead to further increases in stream bank sediment and nutrient contributions to watershed sediment exports (Walsh et al., 2005; Cashman et al., 2018). With limited resources available, all of these factors must be taken into consideration when creating BMPs and TMDLs to ensure that resources spent on watershed mitigation, restoration, and management return maximal results.

## **Chapter 6**

### **CONCLUSIONS**

Sediment fingerprinting revealed that stream banks are a significant, if not dominant source of both sediment and sediment-bound nutrients to the Big Elk Creek, a tributary of the Chesapeake Bay. Stream bank material was ubiquitous in our storm suspended sediments with 50% of the suspended sediment from nine storms being attributed to stream bank sources, by mass. Stream bank nutrient concentrations were significantly lower than those of upland sediments, but still constitute an important source of sediment-bound nutrients to watershed exports due to the high mass loadings of stream bank suspended sediments.

We find that 32% of sediment-bound C, 26% of sediment-bound N, and 32% of sediment-bound P. These results are higher than previous estimates of stream bank contributions to Chesapeake Bay nutrient yields and are comparable with model calibration results from the Phase 6 Chesapeake Bay model. As sediment yields are significantly correlated with peak discharge, larger storms will thus export the most sediment and sediment-bound nutrients. Stream bank contributions also varied temporally depending on hydrologic and climactic factors, with an increase in bank contributions following wintertime freeze-thaw erosion and during high peak discharge events.

Stream bank erosion similarly constituted an important contributor to stream bed sediments, with contributions highest following freeze-thaw erosion during the Winter and early Spring months. Secondary stream bed erosion likely comprises a significant sediment source during late Spring and Summer storms. A decrease in

stream bank contributions to stream bed sediments was observed in June, attributed to the depletion of freeze-thaw derived bank material in the stream beds.

Stream bank contributions to watershed sediment and nutrient yields in the Mid-Atlantic are exacerbated by the ubiquitous presence of legacy sediments in the landscape. Despite this, both legacy and in-channel pollutant sources have been neglected in TMDLs, BMPs, and watershed restoration projects. As climate variability and the frequency of extreme events are projected to increase in the 21<sup>st</sup> century, channel sediment sources must be included in future projects to ensure that restoration and mitigation targets as well as taxpayer dollars are not misallocated. Fortunately, the inclusion of both stream banks and stream beds in the Phase 6 Chesapeake Bay Model suggests that a paradigm shift may be occurring, and channel sources are seriously being considered as a sediment and nutrient sources. Targeting stream banks for restoration and mitigation may be an effective and cost-effective way to reduce pollution to the Chesapeake Bay while also reducing financial burdens on contemporary landowners in the Mid-Atlantic.

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SUPPLEMENTARY INFORMATION

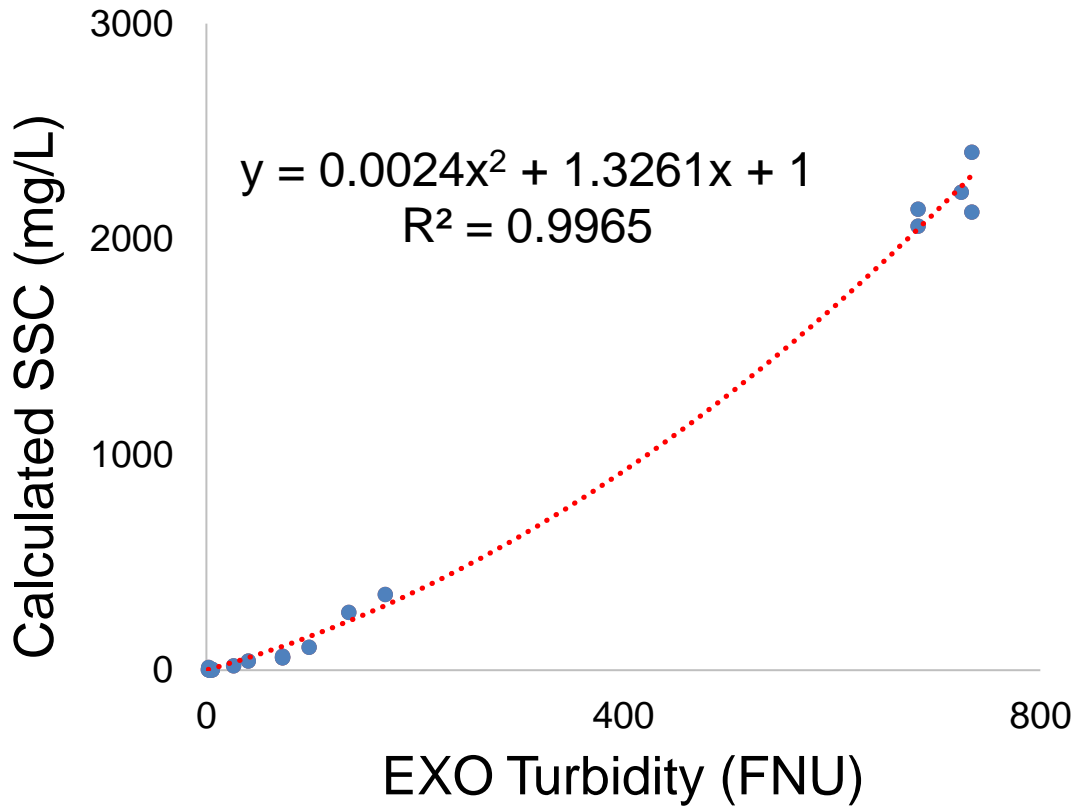


Figure A1: Relationship between sensor turbidity (Formazin Nephelometric Units) to measured suspended sediment concentration ( $\text{mg L}^{-1}$ ).

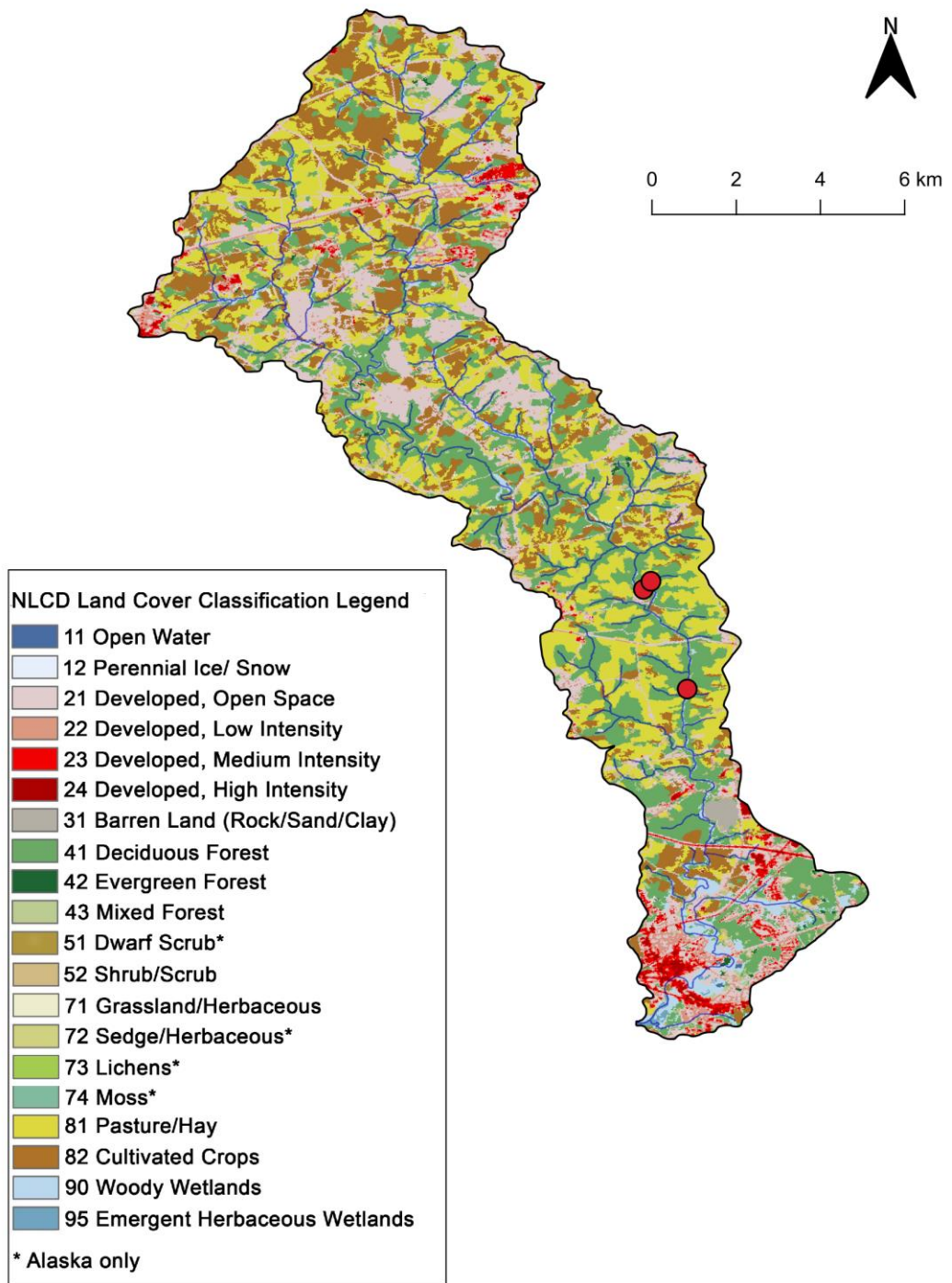


Figure A2: Land use within the watershed, per the NLCD 2011 data. Sampling locations are marked in red.



Figure A3: Discrete storm sampling during the February 11, 2018 event at the Big Elk Creek upstream site.



Figure A4: Passive sampler used to collect storm sediment samples at the Big Elk Creek, downstream site.



Figure A5: Dam remnants at the Big Elk Creek, downstream site. Note remnants of retaining wall in the background.



Figure A6: Sediment sampling at a legacy sediment impacted-stream bank within the Big Elk Creek.



Figure A7: Stream bank erosion at the Big Elk Creek, downstream site following the February 2018 storm events.



Figure A8: Stormflow during the April 16, 2018 event from the Big Elk Creek upstream site.



Figure A9: High suspended sediment concentrations during the July 23, 2018 event from the Big Elk Creek, upstream site.



Figure A10: Channel deposition following the July 23, 2018 event at the Big Elk Creek, upstream site.



Figure A11: A lab member showing how much stream bank erosion was recorded by an erosion pin at the Big Elk Creek downstream site between the date of installation (8/3/2017) and the date of the photo (4/3/2019).

Table A1: Sediment sampling locations. Cropland sampling locations are redacted per the request of the landowners.

<b>Site Name</b>	<b>Site Type</b>	<b>Longitude</b>	<b>Latitude</b>
AGRP1	Agriculture, Pasture	-75.8424	39.70889
AGRP2	Agriculture, Pasture	-75.8378	39.72011
AGRP4	Agriculture, Pasture	-75.8462	39.72987
AGRP5	Agriculture, Pasture	-75.8513	39.72816
SBLS1	Stream Bank	-75.8408	39.71392
SBLS2	Stream Bank	-75.8421	39.71474
SBLS3	Stream Bank	-75.8672	39.73897
SBLS4	Stream Bank	-75.8676	39.73962
SBLS5	Stream Bank	-75.8481	39.72622
BEBT1	Stream Bank	-75.8395	39.7136
BEBT2	Stream Bank	-75.8387	39.71339
SMT1	Stream Bank	-75.8277	39.68675
SMT2	Stream Bank	-75.8272	39.69522
CB	Stream Bank	-75.8826	39.74631
DEVL1	Developed	-75.8263	39.69403
DEVL2	Developed	-75.8277	39.70096
DEVL3	Developed	-75.839	39.70979
DEVL4	Developed	-75.8755	39.73545
DEVL5	Developed	-75.9205	39.76229
DEVL6	Developed	-75.8411	39.71487
FRST1	Forested	-75.8247	39.69469
FRST2	Forested	-75.8416	39.71329
FRST3	Forested	-75.8366	39.71539
FRST4	Forested	-75.8324	39.71894
FRST5	Forested	-75.8498	39.72675
FRST6	Forested	-75.8662	39.73565
FRST7	Forested	-75.8832	39.7486
79 ha tributary Big Elk, upstream	Monitoring location	-75.84	39.72
Big Elk, downstream	Monitoring location	-75.84	39.71
	Monitoring location	-75.83	39.69