INVESTIGATING SPATIAL VARIATIONS IN SEDIMENT ORIGIN USING A STREAMLINED SEDIMENT FINGERPRINTING APPROACH IN A SOUTHERN PIEDMONT WATERSHED

By

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(Under the Direction of David Radcliffe)

ABSTRACT

Sediment fingerprinting is a relatively recent technique capable of determining the origin of suspended sediment. The objective of this study was to examine spatial variations in the origin of suspended sediments and to test a streamlined fingerprinting approach which would reduce the cost. Samples were collected from three tributaries, the outlet of the main stem, and at the middle of the main stem. Two methods to collect suspended sediment samples were compared: a mobile continuous flow centrifuge and automated samplers. A relatively small initial tracer suite consisting of ^{15}N, ^{13}C, TN, and TC was employed in tracer selection. Results using a multivariate mixing model showed that banks contributed the majority of sediment throughout all locations sampled. The use of the streamlined approach should allow for the adoption of sediment fingerprinting as an operational tool for state agencies in the Southern Piedmont wishing to utilize it in TMDL/BMP evaluations.

INDEX WORDS: Sediment Fingerprinting, TMDL, Sediment Load, Uncertainty Analysis

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DEDICATION

I would like to dedicate this thesis to my wife Meggie whose patience with and support of me seem never-ending. Thank you for both starting me down this path and seeing me through it. I love you.

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I'd like to thank everyone whose help was necessary during my time in graduate school and without whose assistance I'd never have finished. Rajith Mukundan deserves my endless praise both for pointing me towards this program and for providing insight for my research whenever needed. My major advisor Dr. David Radcliffe who was willing to entertain my occasionally half conceived explanations (and without whose decidedly prompt edits of this thesis I would never have graduated this quickly) deserves my many thanks as well. I'd like to thank Patrick Gannon for his help in collecting and analyzing samples, this was a two man job in the field and I'd never have collected any data without him. Also, Ken Bradshaw and Dr. Peter Hartell were seemingly always willing to provide me with any help that I needed. Finally, thanks to all the wonderful staff here at the Crop and Soil Science department who make all of our academic pursuits possible and all of the friends I've made. Good luck to all.

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Chapter 1

Introduction and Literature Review

In the United States, about 15% of assessed stream miles are considered threatened or impaired with respect to suspended sediment according to the United States Environmental Protection Agency's (USEPA) 2004 ATTAINS database (USEPA 2008). In the Southeast, many Piedmont streams are considered impaired due to sediment levels. These large concentrations of suspended sediment have an adverse impact on stream biota from primary producers to upper food chain predatory species (Dunne and Leopold 1978). In an effort to reduce sediment loading, Total Maximum Daily Loads (TMDLS) and Best Management Practices (BMPs) have been developed for sediment and runoff control. In an effort to implement TMDLs and BMPs in the Southern Piedmont, research is needed to better identify the source of these suspended sediments.

The Southern Piedmont had elevated rates of erosion during the intensive cotton farming era of 1830-1930 and as a result, channels and floodplains were inundated with the estimated 9.7 km^3 of soil that were eroded in the region (Trimble 1974). In modern times, erosion rates in the Piedmont have waned to levels approaching if not equal to their pre-European settlement rates because agriculture has waned and soil conservation measures have been put in place (Trimble 1974). It is apparent however that the effects of this period are still being felt as fluvial processes continue the task of transporting the *legacy sediments* deposited a century ago.

The North Fork Broad River (NFBR) is in Northeast Georgia. In 1998 it was placed on the 303(d) list for impacted biota and habitat with sediment being the pollutant of concern. In

2004 the USEPA conducted a macroinvertebrate study on the watershed. Based on the results of the study, the watershed was removed from the 303(d) list, however they reported that "habitat concerns are present but not to an extent impacting biota." In 2004 a grant was appropriated to implement BMPs and monitor sediment loads in the NFBR. A subsequent grant in 2007 funded our current research which involves the use of rapid geomorphic assessments and sediment fingerprinting to examine channel stability and determine the source contributions of suspended sediment.

In terms of stream channel equilibrium and geomorphic analysis, Mukundan and his coworkers (2009) showed that 69% of stream reaches in the NFBR were unstable, with an elevated rate of bank scour and channel degradation. The sediments being eroded in these unstable channels are primarily legacy sediments deposited during the intensive cotton farming era. The use of Rapid Geomorphic analysis proved a useful tool in determining the stability class of individual reaches and their potential for sediment contribution.

In terms of sediment fingerprinting, 60% of suspended sediment originated from eroding stream banks, 23 to 30% from upland subsurface sources (construction sites, unpaved roads), and 10 to 15% from pastures (Mukundan 2009). Sediment fingerprinting involves establishing source "fingerprints" made up by a suite of various chemical and physical characteristics that provide a unique signature. Upon establishing the source fingerprints, suspended sediment is collected and analyzed for those same characteristics. Using statistical models, it is then possible to determine relative contributions from source types.

The objective of this study was twofold. First we wanted to examine several sub basins within the NFBR to determine our ability to utilize the fingerprinting technique to achieve a higher resolution in terms of sediment origination within the overall basin. Second, it was our intention to somewhat streamline the technique in order that it be easily adopted by state agencies developing and implementing sediment TMDLs. In addition to streamlining, we wanted to make it as cost and time effective as possible, recognizing that the traditionally large cost of sediment fingerprinting made it impractical for widespread use by state agencies.

Literature Review

Suspended Sediment

Erosion can be defined as “the wearing away of the land surface by detachment and movement of soil and rock fragments through the action of moving water and other geological agents” (Cline et al., 1981). With streams and water quality in mind, erosion is an important process in that it is the genesis of sediment which ultimately is suspended in the water column and carried downstream. It has long been a problem agriculturally in that erosion leads to a loss of fertile topsoil. The southern Piedmont of the U.S. is a good example of how erosion can devastate a landscape in terms of agricultural productivity. Today, in the southern Piedmont and around the world, sediment is also seen as a problem of water quality which affects not only the stream biota but also the human population.

Suspended sediment is the portion of the total sediment load that is carried in the water column. It can be broken into two components; one is washload or the colloidal fraction of suspended load, and the other consists of suspended sands. It is differentiated from bedload which consists of sands and larger material transported along the bed of the stream (USEPA 2011a). These sediments can originate from cultivated fields or grasslands, forests, construction sites, roadways, urban areas, stream channels or active gullies (Robinson, 1979). They may travel directly from the source of erosion to the channel or they may be eroded and then settle out before reaching the stream only to make the rest of their voyage at a later date.

Suspended sediment can affect stream biota in a number of ways. Excessive turbidity can damage trout populations by both encumbering their ability to predate by limiting their vision, by covering the gravel substrate used to lay eggs, and by clogging the gills during early development (Dunne and Leopold, 1978). Sediments may also carry any number of pollutants which are adsorbed to the surfaces of colloidal particles. The reduction in clarity caused by suspended sediment can be measured in Nephelometric Turbidity Units using light scattering instruments (Radcliffe 2002). It is generally accepted that prolonged elevations of suspended sediment concentrations (SSC) are detrimental to biotic health.

Total Maximum Daily Loads (TMDLs)

A TMDL is a calculation of the total amount of a pollutant that a waterbody can receive in a day and still meet water quality standards. The origin of the TMDL can be found in section 303(d) of the 1972 clean water act. This law requires states, territories, and tribes to develop lists of impaired water, then prioritize and develop TMDLs for them (USEPA, 2011b). There are currently 40,235 impaired water bodies in the US (USEPA 2011b).

The purpose of a TMDL as a pollutant load limit is to develop a plan of action to limit that pollutant called a TMDL implementation plan (USEPA 2011c). Numerous techniques are used in the development of a TMDL including mass balance calculations and complex watershed modeling. The EPA summarizes TMDL development as follows (USEPA2011c):

- Selection of the pollutant to consider
- Estimation of the waterbody assimilative capacity (i.e., loading capacity)
- Estimation of the pollutant loading from all sources to the waterbody

- Analysis of current pollutant load and determination of needed reductions to meet assimilative capacity
- Allocation (with a margin of safety) of the allowable pollutant load among the different point and nonpoint pollutant sources in a manner that water quality standards are achieved

Once a TMDL (target load) has been determined, the implementation plan must be developed. This involves creating a plan which describes the strategy to be employed in reducing the impairment of concern. This can include a myriad of actions including but not limited to stream restoration, BMP implementation and enforcement, riparian buffer creation and protection, and public outreach (Benham and Zeckoski, 2009). According to the Clean Water Act, states are responsible for the development of TMDL plans; however they must be submitted to the EPA for approval. The process of developing a TMDL can take anywhere from 2-5 years. This period of time allows for the collection of monitoring data which may be used to remove the waterbody from the impaired list (USEPA 2011c).

Rapid Geomorphic Assessments (RGA)

A study was conducted in the North Fork Broad River (NFBR) watershed starting in 2009 (Mukundan et al. 2010) with the intent of determining the sediment contributions from different land use types for the main stem of the NFBR. The study found that around 65% of the suspended sediment was of bank origin, 25% from upland subsurface inputs, and 13% from pastures. This study, as well as ours, used the concept of channel evolution in streams developed by Andrew Simon and his associates (Simon and Hupp, 1986; Simon 1988). Simon's model was created in western Tennessee in an attempt to understand stream channel response to channelization in that region. It was noted that upstream of disturbance (channelization) degradation was occurring with bed levels lowered up to 6 meters. Simon created a six-stage model which documented the progression from pre-disturbance stable to post disturbance stable (or pre and post equilibrium conditions).

The model is described in detail by Andrew Simon (1988) . The first stage of the model is the pre modified stream. This stage is the result of natural processes and banks are generally stable with very little mass wasting. The second stage is the constructed stage. This stage involves restructured banks or channel repositioning. It is considered the transition stage to more unstable stages. The third stage is the degradation stage. In this stage, there is a rapid erosion of the stream bed resulting in incision and an increase in the height of channel banks. Widening has not yet begun as the stream is still in the process of steepening the angle of the banks to the point where they exceed their critical angle. The fourth stage is the threshold stage. In this stage the banks have met their critical height and angle threshold and are beginning to widen and experience mass wasting. Bank faces may be near vertical due to erosion of bank toes. The fifth stage is the aggradation stage. In this stage the channel bed has begun to aggrade. In addition to bed aggradation, banks surfaces will often have sands deposited on them. Widening is still occurring in the upper bank however, down slope of the upper bank, failed material is slumped and forming a distinguishable lower bank with a much less severe angle. The sixth stage is the restabilized stage, representing a new equilibrium in terms of sediment.

Rapid geomorphic assessments (RGAs) are used to determine the stage of channel evolution and overall stability. The RGAs carried out in this study followed the channel stability ranking scheme (Klimetz and Simon, 2007). There are nine criteria used in performing an RGA. These are: primary bed material, bed/bank protection, degree of channel incision (percentage), degree of downstream constriction (percentage), dominant bank erosion type (fluvial vs. mass wasting), percentage of each bank failing, established riparian woody buffer (percentage), occurrence of bank accretion (percentage) , and finally the stage of channel evolution from Simon's model. A score above 20 indicates a very unstable reach; a score below 10 indicates a reach is quite stable.

Other methods of stream classification do exist however. Perhaps the most prominent is the Rosgen system (Rosgen 1985, 1994). The Rosgen system seeks to develop a stream classification system based on channel morphology. There are eight variables affecting morphology: channel width, depth, slope, roughness, water velocity (ft/s) and discharge (ft3/s), and sediment load and size. The system has 3 levels of classification. The first level is a broad morphological description and seeks to classify a stream into a general major stream type by using a combination of slope, cross-section, and plan view. The second level is a continuation of the first and seeks to further group streams into homogenous groups based on slope and channel material particle size. The third level is the most detailed and seeks to classify the stream based on its current "state". The is accomplished by using a number of criteria including vegetation, flow regime, debris, depositional features, meander patterns, valley and channel confinement, streambank erodibility, and channel stability. Rosgen (1994) also describes channel evolution in terms of the same eight variables illustrating how they respond in response to some change in channel conditions and how the stream classification will adjust accordingly.

Sediment Fingerprinting

While geomorphic analysis allows us to determine the stability of stream channels, it is sediment fingerprinting that is able to illuminate actual provenance of sediment suspended during storm flow. There have been numerous sediment fingerprinting studies in the past and the method has proven itself an effective tool in determining sediment source type and spatial origin (Walling, 2005). The technique involves the characterization of source types based on chemical, physical and/or biological properties establishing individual source "fingerprints". The tracers used must be measurable in both source soils and sediment and must be conservative in that they don't undergo any chemical alterations between generation and delivery. Properties used include sediment color (Grimshaw and Lewin, 1980), plant pollen (Brown, 1985), mineral magnetic properties (Walden et al., 1997), rare earth elements (Kimoto et al., 2006), fallout radionuclides (Collins and Walling, 2002; Nagle and Ritchie, 2004; Walling, 2005; Mukundan et al., 2010), and stable isotopes of C and N (Papanicolaou et al., 2003; Fox and Papanicolaou, 2007), and Fatty Acid Methyl Esters (Banowetz et al., 2006).

^{137}Cs is a fallout radionuclide which was deposited atmospherically during nuclear weapons testing and to a lesser extent following Chernobyl. It has a half life of 30.2 years. Due to its surficial deposition and limited mobility, it makes an excellent tracer in terms of discriminating between surface and subsurface soils. Other radionuclide tracers include beryliium-7 (^{7}Be) and lead-210 (^{210}Pb). While not a product of weapons testing, ^{210}Pb has proven a useful tracer with behavior similar in nature to that of ^{137}Cs. (Zapata, 2003)

Whereas radioisotopes rely on atmospheric deposition and elemental tracers rely on (in most cases) parent material, stable isotopes are based on biogeochemical cycling. (Papanicolaou and Fox, 2003). During cycling, organisms exhibit a preference for the lighter isotopes. This preference leads to the enrichment of the lighter isotopes in the soil and the "fractionation" or alteration of the isotopic ratios. The compositions are usually expressed in terms of δ values which represent a difference from a standard in parts per thousand (Peterson and Fry, 1987). Plant cover, land use, and land management all affect the isotopic signature of soils (Fox and Papanicoloau, 2007).

In Mukundan (2010), it was found that distinct ^{15}N signatures were quite apparent for the sediment sources in the study (stream banks, forests, pastures, construction sites/dirt roads). Pasture soils exhibited the highest ^{15}N value. Enrichment in pasture soils is due to plant preference for ^{14}N, then the subsequent removal of biomass by both the harvesting and consumption of grasses, and the addition of manures. Banks exhibited the next highest ^{15}N value. Enrichment in the banks is due primarily to landscape position. Their proximity to the water table leads to frequent anaerobic conditions. Anaerobic microbes prefer ^{14}N during denitrification and therefore leave the soil enriched in ^{15}N. Also, it has been observed that enrichment tends to increase with age and therefore depth in the profile for both ^{15}N and ^{13}C (Billings et al., 2006). Unpaved roads and construction sites had relatively low enrichment due to less biological activity in these exposed sub soils. Forest soil ^{15}N values were relatively stable, meaning the values did not deviate much from the standard. This is thought to be due to the recycling of forest organic matter which has been depleted in ^{15}N back into the soil, limiting enrichment with time (Billings and Richter, 2006).

In our previous study here, (Mukundan et al., 2010) the radioisotope ^{137}Cs and the stable isotope N15 were selected as tracers using the tracer selection process described in Collins and Walling (2002). This purpose of this study was to determine the spatial origin of sediment in the North Fork Broad River (NFBR). Three potential sources were identified: pastures, upland subsoil sources such as unpaved roads/construction sites, and stream banks. It was hypothesized that the origin of much of the suspended sediment was the banks of the stream. These banks largely consisted of floodplain deposits of previously eroded sediment from cotton agriculture in the 19th century termed *legacy sediment*. It was determined that around 60% of the suspended sediment in the main stem was of bank origin, 15% of pasture origin, and 25% from upland subsoil sources.

Most fingerprinting studies use physical or chemical signatures to identify sediment sources. However, biological tracers can be utilized to the same effect. Fatty acid methyl esters (FAME) utilize the fatty acids found in soil microbiological communities and can be used to generate unique fingerprints for different soils (Kennedy, 1998; Ibekwe and Kennedy, 1999). In Bannowetz et al. (2006) three soil categories of differing land use (field drainage, agricultural, and wooded riparian) were classified with a 4.6% error rate using quadratic discriminate analysis. Given the large number of fatty acids present in a soil sample, multivariate techniques including cluster analysis and principal component analysis are essential to the utilization of FAMEs in sediment fingerprinting and their use is outlined in Kennedy (1998).

Walling et al. (1993) proposed the utilization of multi-parameter composite fingerprints to differentiate between sediment sources particularly when the number of sources is greater than two. Collins and Walling (2002) performed a study in multiple contrasting river basins in the UK and Africa. They found that a combination of multiple diagnostic tracers used in multivariate mixing models was best in terms of discriminatory power. However, it was also noted that tracer "suites" were not always consistent between basins. In their paper, a process was outlined for the selection of sediment tracer properties to be used in a fingerprinting study. This technique has been widely adopted in the field and based on the work of several previous attempts at statistical verification of composite fingerprints (Collins et al. 1996, 1998) The process involves statistical testing of properties both individually using the Kruskal _Wallis H-test (to check for redundancy) and as a group through discriminant function analysis (DFA). In

DFA, the minimization of Wilk's Lamda is used in a stepwise selection algorithm to choose the composite fingerprint,

Once the composite fingerprint has been selected, it is possible to determine source contributions using statistical modeling. "Mixing" models or more accurately "unmixing" models are employed in order to estimate the contribution from individual sediment sources. At their simplest, these mass balance models rely on one tracer and two sources yielding a trivial algebraic solution. With more than one tracer, the equations used become an over determined matrix with more information than is needed to solve. (Davis and Fox, 2009). The multivariate mixing model (Collins et al. 1996; Walling et al. 1999; Walling 2005; Mukundan 2010) involves minimizing the sum of squares of residuals between predicted tracer values for each source in sediment samples and those observed and is an optimization problem. In his study, Mukundan (2010) compared the more widely adopted MVMM to End Member Mixing Analysis (EMMA). End Member Mixing Analysis (EMMA) has been used with some success in hydrologic studies (James and Roulet, 2006; Burns et al. 2001) and relies on principal component analysis (PCA) for dimensionality reduction in terms of tracers. Mukundan found both approaches yielded similar results.

Over the years, mixing models have begun to account for model uncertainty in the following areas: variability of each relative tracer, error in characterizing sources, measurement error, uncertainty during the erosion process, and weighting the relative persistence of multiple erosion processes at a single source (Davis and Fox, 2009). In Krause et al. (2003), tracer values were represented using the Student's t-distribution rather than mean or median values for both source and sediment sample values. Instead of a simple optimization, the distributions were sampled 1000 times and the system of equations solved for each realization. The resulting fractional source contributions were then used to represent the uncertainty associated with the use of both spatially and temporally limited samples.

In Evrard et al. (2011), a fingerprinting study in the French Alps was undertaken. A similar approach was used in terms of applying distributions to tracer data and utilizing Monte Carlo sampling in the mixing model. A mean goodness of fit (GOF) was used and only fractional source contributions which proved robust enough based on this (GOF > 0.80) were accepted. A study in southeastern Australia (Motha et al. 2003) again utilized a similar approach to uncertainty in source tracer values. Here a GOF index of 0.95 was used as a tolerance criterion.

In the development of sediment TMDLs, perhaps the most difficult aspect is determining the source. Using standard approaches such as GIS based modeling and field studies involving erosion pins yields results of an indirect nature. These approaches may not take into account sediment storage down slope from zones of erosion. Direct analysis of the suspended sediment itself and the use of the techniques highlighted above provide the most accurate picture of sediment origin in a watershed.

The objective of this study was twofold. First we wanted to examine several sub basins within the NFBR to determine our ability to utilize the fingerprinting technique to achieve a higher resolution in terms of spatial variations in sediment origin within the overall basin. Second, it was our intention to somewhat streamline the technique in order that it be easily adopted by state agencies developing and implementing sediment TMDLs. In addition to streamlining, we wanted to make it as cost and time effective as possible, recognizing that the traditionally large cost of sediment fingerprinting made it impractical for widespread use by state agencies.

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CHAPTER 2

INVESTIGATING SPATIAL VARIATIONS IN SEDIMENT ORIGIN USING A STREAMLINED SEDIMENT FINGERPRINTING APPROACH IN A SOUTHERN PIEDMONT WATERSHED[1]

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Abstract

Sediment fingerprinting is a relatively recent technique, capable of determining the origin of suspended sediment. In this follow up study we investigated sub basins within a larger watershed we previously examined. The objective was to examine spatial variation in the origin of the suspended sediments and to test a streamlined fingerprinting approach which would reduce the cost. Samples were collected from three tributaries, the outlet of the main stem, and at the middle of the main stem. Two methods to collect suspended sediment samples were compared: a mobile continuous flow centrifuge and automated samplers. A relatively small initial tracer suite consisting of ^{15}N, ^{13}C, TN, and TC was employed in tracer selection. The pool was tested for discriminatory power in another watershed in the region and found to provide similarly positive results indicating its possible applicability as an inexpensive regional tracer suite. Tracer concentrations were obtained through a single mass spectrometry analysis requiring less than one gram of sediment. Results using a multivariate mixing model showed that banks contributed the majority of sediment throughout all locations sampled and that in tributaries it was an even more dominant source. The use of the streamlined approach should allow for the adoption of sediment fingerprinting as an operational tool for state agencies in the Southern Piedmont wishing to utilize it in TMDL/BMP evaluations.

Introduction

In the United States, about 15% of assessed stream miles are considered threatened or impaired with respect to suspended sediment according to the United States Environmental Protection Agency's 2004 ATTAINS database (USEPA 2008). In the Southeast, many Piedmont streams are considered impaired due to high sediment loads. In an effort to reduce sediment loading, Total Maximum Daily Loads (TMDLs) and Best Management Practices (BMPs) have been developed for sediment and runoff control. Research is needed in the Southern Piedmont (AL, GA, SC, NC, and VA) to better identify the source of these suspended sediments.

The Southern Piedmont had elevated rates of erosion during the intensive cotton farming era of 1830-1930 and as a result, channels and floodplains were inundated with the estimated 9.7 km^3 of soil that were eroded in the region (Trimble, 1974). In modern times, erosion rates in the Piedmont have waned to levels approaching, if not equal, to their pre-European settlement rates because row-crop agriculture has decreased, soil conservation measures have been put in place, and much of the land is forested. It is apparent, however, that the effects of this period are still being felt as fluvial processes continue the task of resuspending and transporting the *legacy sediments* deposited a century ago and urbanization increases stream power (Carter et al., 2009).

Suspended sediment can affect stream biota in a number of ways. Excessive turbidity can damage trout populations by both limiting their ability to see and predate, by covering the gravel substrate used to lay eggs, and by clogging the gills during early development (Dunne and Leopold, 1978). Sediments may also carry adsorbed pollutants

Sediment fingerprinting is a relatively recent technique capable of directly determining the source of suspended sediment in streams. There have been numerous sediment fingerprinting studies in the past and the method has proven to be an effective tool in determining sediment source type and spatial origin (Walling, 2005). The technique involves the characterization of source types based on chemical, physical and/or biological properties establishing individual source "fingerprints". The tracers used must be measurable in both source soils and sediment and must be conservative in that they don't undergo any chemical alterations between generation and delivery. Properties used include sediment color (Grimshaw and Lewin, 1980), plant pollen (Brown, 1985), mineral magnetic properties (Walden et al., 1997), rare earth elements (Kimoto et al., 2006), fallout radionuclides (Collins and Walling, 2002; Nagle and Ritchie, 2004; Walling, 2005; Mukundan et al., 2010), stable isotopes of C and N (Papanicolaou et al., 2003; Fox and Papanicolaou, 2007), and fatty acid methyl esters (Banowetz et al., 2006).

Cesium 137 is a fallout radionuclide which was deposited atmospherically during nuclear weapons testing and to a lesser extent following Chernobyl (Walling, 2005). It has a half life of 30.2 years. Due to its surficial deposition and limited mobility, it makes an excellent tracer in terms of discriminating between surface and subsurface soils. Other radionuclide tracers include beryliium-7 (^{7}Be) and lead-210 (^{210}Pb). A product of cosmogenic radiation, ^{210}Pb has proven a useful tracer with behavior similar in nature to that of ^{137}Cs. (Zapata, 2003)

Whereas radioisotopes rely on atmospheric deposition and elemental tracers rely on (in most cases) parent material, stable isotopes are based on biogeochemical cycling (Papanicolaou and Fox, 2003). During cycling, organisms exhibit a preference for the lighter isotopes. This preference leads to the enrichment of the heavier isotope in the soil and the “fractionation” or alteration of the isotopic ratios. The concentrations are usually expressed in terms of δ values which represent a difference from a standard in parts per thousand (Peterson and Fry, 1987). Plant cover, land use, and land management all affect the isotopic signature of soils (Fox and Papanicoloau, 2007).

A previous study (Mukundan et al., 2010) reported on sediment sources in the North Fork Broad River (NFBR), a typical rural stream in the Piedmont region of Georgia. The radioisotope ^{137}Cs and the stable isotope ^{15}N were selected as tracers using the tracer selection process described in Collins and Walling (2002). Three potential sources were identified from an initial pool of six (forests, pastures, unpaved roads, row crops, construction sites, and banks): pastures, exposed subsoil sources consisting of unpaved roads/construction sites, and stream banks. Forests and row crop agriculture were found not to contribute (row crop due to its very small land use percentage) and the study was unable to discriminate between dirt roads and construction sites due to the inherent similarities in terms of tracer values (both are exposed subsoils). It was hypothesized that the origin of much of the suspended sediment was the banks of the stream. These banks largely consisted of floodplain deposits of previously eroded sediment from cotton agriculture in the 19th century termed *legacy sediment*. Although ^{137}Cs could only distinguish pasture from other sources, distinct ^{15}N signatures were apparent for all three principal sediment sources. Pasture soils exhibited the highest ^{15}N value, followed by banks, and then subsoils. Overall, the study found that approximately 60% of the suspended sediment in the main stem was of bank origin, 15% of pasture origin, and 25% from upland subsoil sources.

In addition to utilizing the fingerprinting technique, Mukundan et al (2010) performed Rapid Geomporphic Assessments (RGAs) to examine channel stability. These assessments use the concept of channel evolution in streams developed by Andrew Simon and his associates (Simon and Hupp, 1986; Simon 1988). Geomorphic assessments are an important compliment to fingerprinting because while land use data is generally available, little is known about channel conditions. The results of the RGAs were that both the main stem and several of the tributaries of the NFBR had incised and relatively unstable channels. It is worth noting that there are other methods of stream classification available with the Rosgen system (Rosgen, 1985, 1994) being the most prominent.

In a presentation given at the 2010 Land and Sea Grant National Water Conference, Walling (2010) proposed several measures to improve sediment fingerprinting. One suggestion was to transform sediment fingerprinting from its current use as a research tool into an operational tool. In order to accomplish this, Walling stated that well defined protocols must be developed for those wishing to adopt the technique. Walling also suggested the use of small volume samples collected by automated samplers and extracted on filter paper as an alternative to traditional sampling methods. In addition, he encouraged the use of Monte Carlo simulations for uncertainty analysis.

The objective of this study was to extend our earlier work on the NFBR in two ways. First we wanted to examine several sub basins within the NFBR to look for spatial variations in the origins of suspended sediment. While the initial study sampled suspended sediment at the main stem outlet, it was not clear if there were variations in source contributions throughout the NFBR or if the same general trend would emerge. Second, it was our intention to streamline the technique so that it could be adopted by state agencies developing and implementing sediment TMDLs. We wanted to make it as cost and time effective as possible, recognizing that the traditionally large cost of sediment fingerprinting used as a research tool made it impractical for widespread use as an operational tool by state agencies.

Materials and Methods

Watershed

The North Fork Broad River (NFBR) is in Northeast Georgia (Fig. 2.1). In 1998 it was placed on the 303(d) list for impacted biota and habitat with sediment being the pollutant of concern. In 2004 the USEPA conducted a macroinvertebrate study on the watershed. Based on the results of the study, the watershed was removed from the 303(d) list, however they reported that "habitat concerns are present but not to an extent impacting biota." In 2004 a grant was awarded to implement BMPs and monitor sediment loads in the NFBR. A subsequent grant in 2007 funded our current research which involves the use of rapid geomorphic assessments and sediment fingerprinting to examine channel stability and determine the source contributions of suspended sediment. Three sub basins of the NFBR were selected for this study: Tom's Creek (61% forest, 38% pasture, 1% urban), Clarke's Creek (59% forest, 39% pasture, 2%urban), and Davis Creek (80% forest, 17% pasture, 3% urban) (Fig. 2.1). Selection was based on sub basin size, land use, and accessibility. Rainfall data was collected from the USGS gauging station at Panther Creek near Toccoa GA.

Sampling

In our previous study (Mukundan et al., 2010), spatially distributed composite soil samples were taken from about 150 sites which represented the potential sediment sources within the watershed. This sample data set was again utilized in the current study. The previous results indicated that there was no contribution from forests or row crops (due to lack of runoff and lack of total land use area, respectively) so this study exluded those land uses as sources. Recapping briefly how these samples were collected, upland soil samples were collected from the upper 0-2 cm depth of potential sources. Bank samples were collected in areas of the channel visually identified as actively eroding by scraping the face of the bank and collecting samples from the surface of the stream to a height about 1 m above the stream.

The majority of suspended sediment is transported by streams during storms and as such it is necessary to sample during storm events. Conventionally, fingerprinting has required pumping large volumes of water (100-400 L) and transporting them for centrifugation (Walling et al., 1993). This has been due to the large mass requirements (20-100 g) of radionuclide tracers as well as the mass necessary for multiple analyses and particle size analysis in a conventional tracer suite (10-50 g). This provides a composited sample with contributions from multiple sources. In this study suspended sediment samples were collected using two techniques:

pumping water out of the stream and passing it through a continuous flow centrifuge collector mounted at the back of a pick-up truck, and using automated ISCO samplers (Teledyne Technologies, Inc., Thousand Oaks, CA) to collect water samples which were then filtered in the lab. The centrifugation method of sampling allows for a large sample mass. Automated samplers were used (in addition to centrifugation sampling) in our study for several reasons. First, the analysis for the tracers in our study only required 50-100 mg at most and therefore the large masses associated with analysis of ^{137}Cs were unnecessary. Second, the use of automated samplers allowed multiple samples to be collected along a storm hydrograph at a site and simultaneous sampling on multiple tributaries, providing a more detailed picture of sediment dynamics within the system. Centrifuge samples were air-dried and sieved at 2 mm, then analyzed for particle size. Automated samples were taken at 1 hour intervals after reaching a pre-determined stage threshold which was generally 15 cm above baseflow level. Samples were composited based on hydrograph readings and suspended sediment concentrations so that each section of the hydrograph was represented by and individual sample (rising, peak, recession) and that adequate sample was available for analysis. In lieu of particle size analysis, samples were poured through a 0.05-mm sieve to remove sand so that tracer results would be expressed in terms of fines. Vacuum filtration and 0.45 µm glass fiber filters were used to remove sediment. Sample dates, locations, methods, rainfall and turbidity are provided in Table 3.5. Turbidity values were measured in the field at the time of sampling for centrifuged samples and in the lab for ISCO samples using a HACH 2100 turbidimeter (HACH Co. Loveland Colorado).

Tracers

Because our previous study had shown the ability of ^{15}N and total carbon (TC) to discriminate sources, we decided to expand their use in this study. The analysis used (isotope mass spectrometry) requires a small enough mass (< 50 g) so that 1-liter samples from an automated sampler suffice and the analysis is relatively inexpensive making this an excellent candidate for state agency adoption. Because the analysis also yields ^{13}C and total nitrogen (TN) data, these tracers were included in the initial pool and the selection process outlined in Collins and Walling (2002) was utilized. For the process, Excel Stat (a Microsoft Excel plug-in) was utilized for statistical analysis. Each individual tracer was subjected to the Kruskall-Wallis H-test, tracers remaining were then normalized by dividing by the maximum value for the group, following that stepwise discriminant function analysis was employed to determine the final tracer suite. The Kruskall-Wallis H-test is a non parametric equivilant of ANOVA and is used to test the individual ability of each tracer to discriminate sources so that tracers unable to discriminate are not included in the initial tracer pool. Discriminate analysis can be thought of as a regression analysis where the dependant variable is group membership. By finding a linear combination of variables that maximize between group variance while minimizing within group variance, observations can be classified into groups.

In an effort to test the ability of the tracer suite in multiple watersheds, the South Fork Broad River (SFBR) watershed which is located about 30 miles south of the NFBR was also sampled and analyzed using DA. The SFBR has an area of about 563 km^2 and its land use is as follows: urban 2%, pasture 43%, and forest 55%. A total of 40 samples were collected in the summer of 2010 with 10 samples taken for banks, 10 samples for forest, 10 for pasture, and 10 for exposed sub-soils (unpaved roads and road ditches). The sampling method was the same as with the NFBR with composited samples taken to a depth of about 2 cm, air dried, sieved, and analyzed for particle size.

Fox and Papanicolaou (2008) described the applicability of ^{15}N to fingerprint sediment coming from sources as affected by land-use, management, geomorphology, and soil depth at a watershed scale. Values for both ^{15}N and ^{13}C were calculated in the same manner. The stable isotope is expressed relative to the atmospheric isotope in δ notation indicating the difference between the sample isotopic ratio (*Rsample*) and the ratio in the standard (*Rstd*):

$$\delta X = \left(\frac{Rsample}{Rstd} - 1 \right) 10^3 \qquad [1]$$

where δX is expressed in parts per thousand.

Stable isotope analysis was performed by the analytical chemistry lab at the Odum School of Ecology, University of Georgia. For source samples, the analysis was performed using a few milligrams out of 5 to 10 g of fine soil that was ground and homogenized in a ball mill. Samples were weighed and placed in tin capsules for analysis. The laboratory used a Carlo Erba NA 1500 CN Analyzer coupled to a Thermo-Finnigan Delta V Mass Spectrometervia Thermo-Finnigan Conflo III Interface. The standards used in the calculation of delta values were the concentration of the heavy isotope found naturally in air for ^{15}N and the Chicago PDB Marine Carbonate Standard for ^{13}C. The same process was utilized for centrifuged sediment samples. For filtered samples, the sediment was removed from the filter and ground with a mortar and pestle before analysis.

Total Carbon (TC) was found to be an adequate replacement for ^{137}Cs based on correlation (R^2 = 0.67). As well as being less expensive, TC has the same low mass requirement as ^{15}N (<50 mg). Total Nitrogen (TN) was also used. Initially it was found that the C/N ratio was also effective at discrimination however, it was not used because property ratios are not linearly additive and therefore should be avoided in linear mixing models (Walling, 2005). A known issue in fingerprinting studies is the variance associated with soil and sediment sample particle size distributions when samples are collected in a range of geographic locations. In order to account for this, textural analysis was performed on all soil and centrifuged sediment samples. Following the analysis, the elemental tracers (TN and TC) were expressed in terms of the fines by multiplying the tracer value by the inverse of the fine fraction. This ensured that the sediment samples and the soil samples collected from the banks and uplands were comparable. In our case, only TC and TN needed particle size correction. The stable isotopes ^{13}C and ^{15}N are ratios (isotopic ratios don't pose the same issues with linear mixing models) and therefore not dependant on particle size (Mukundan et al., 2010). Samples collected via automated samplers were first poured through a 0.05mm sieve in order to avoid particle size analysis on very low mass samples (there was generally less than one gram) and to still express the results in terms of the fine fraction.

Mixing Model and Uncertainty

Relative source contribution of suspended sediment was estimated by using a multivariate mixing model (Collins et Al., 1998; Owens et al., 1999; Walling et al., 1999). The method of least squares was used for deriving the source proportions by minimizing the residual sum of squares for the *n* tracer and *m* sources:

$$RSS = \sum_{i=1}^{n} \left[\frac{C_{sed\,i} - (\sum_{s=1}^{m} C_{s\,i} . P_s)}{C_{sed\,i}} \right]^2 \qquad [2]$$

where,

RSS = the residual sum of squares

$C_{sed,i}$ = the concentration of the tracer i in the sediment

$C_{s,i}$ = the mean concentration of the tracer property i in the source group s

P_s = the relative proportion from source group s

In order to examine uncertainty in both source tracer values and sediment tracer values, Pallisades @RISK optimizer software was used. Rather than using a mean or median value for tracer values in the model, this approach uses a distribution. The software was used to fit a distribution to each group of tracer values for each source. Then a distribution was fit for each stream sampling site's sediment tracer values. Selection of available distributions which were generated and displayed in order of descending goodness of fit, was based on the chi-squared statistic and probability-probability and quantile-quantile plots. Following this, a Monte Carlo simulation was performed and the model was solved 10,000 times with each solution being generated from a different randomly selected set of tracer values from the distributions. Some solutions to the model can be unrealistic and in order to retain only robust solutions, a goodness of fit criteria of greater than 0.80 was utilized (GOF = 1-RSS) following the procedure used in Motha et al. (2003).

Rapid Geomorphic Assessments

Rapid geomorphic assessments (RGAs) are used to determine the stage of channel evolution and overall stability. The RGAs carried out in this study followed the channel stability ranking scheme of Klimetz and Simon (2007). There are nine criteria used in performing an RGA. These are: primary bed material, bed/bank protection, degree of channel incision (percentage), degree of downstream constriction (percentage), dominant bank erosion type (fluvial vs. mass wasting), percentage of each bank failing, established riparian woody buffer (percentage), occurrence of bank accretion (percentage), and finally the stage of channel evolution from Simon's model. A score above 20 indicates a very unstable reach; a score below 10 indicates a reach is quite stable. The first stage of the model is the pre modified stream. This stage is the result of natural processes and banks are generally stable with very little mass wasting. The second stage is the constructed stage. This stage involves restructured banks or channel repositioning. It is considered the transition stage to more unstable stages. The third stage is the degradation stage. In this stage, there is a rapid erosion of the stream bed resulting in incision and an increase in the height of channel banks. Widening has not yet begun as the stream is still in the process of steepening the angle of the banks to the point where they exceed their critical angle. The fourth stage is the threshold stage. In this stage the banks have met their critical height and angle threshold and are beginning to widen and experience mass wasting. Bank faces may be near vertical due to erosion of bank toes. The fifth stage is the aggradation stage. In this stage the channel bed has begun to aggrade. In addition to bed aggradation, banks surfaces will often have sands deposited on them. Widening is still occurring in the upper bank however, down slope of the upper bank, failed material is slumped and forming a distinguishable lower bank with a much less severe angle. The sixth stage is the restabilized stage, representing a new equilibrium in terms of sediment.

Davis creek is located in the upper half of the NFBR (Figure 2.1). Rapid Geomorphic Assessments (RGAs) were carried out on five reaches of Davis creek on April 26, 2010. RGAs were performed on Tom's Creek and Clarke's Creek in 2008. It is preferable to perform an assessment prior to the spring growth of grasses and leaves, however the assessments at Davis creek were performed under these conditions and required more attention and time to perform.

Reaches were chosen to be representative and varied in length from 300 to 400 m. Spatial coordinates were recorded and each reach photographed for documentation. Also, bed samples were collected for later particle size distribution analysis.

Primary bed material was determined visually, as were the presence of bed/bank protection. The degree of incision was determined by measuring the depth of the stream at the thalweg and dividing that by the average height of the bank from the top to the toe. Constriction was determined by measuring channel width at the upstream and downstream ends of the reach and determining their relative differences. Dominant stream bank erosion processes were determined visually for both the left and right bank as well as the percentage of failing banks. These may be either fluvial (undercutting) or mass wasting (movement of large amounts of bank sediment at once). In order to classify a bank as dominated by mass wasting, 50% or more of the faces must exhibit this process. Vegetative cover was determined by judging the percentage of each bank with established woody vegetation. Grasses tend to be annual and provide no protection during winter months (Klimetz and Simon, 2007). Final index values were determined by tallying each of the scores from the nine categories.

Results

Spatial Variations in Source Contributions

As previously mentioned, the tracer selection process consisted of two steps: the Kruskall-Wallis H-test and multivariate discriminant function analysis (DA). Tracer statistics, distributions of the tracer data sets, and results of the Kruskall-Wallis H- test which illustrated the ability of the individual tracers to discriminate between source types within the NFBR are provided in Table 2.1. The distributions listed describe the best possible fit to the data using @ RISK software and were selected based on their Chi-squared statistic and P-P plots. Table 2.2

displays the tracer statistics and results of the Kruskall-Wallis H-test from the SFBR and illustrate the similarity of the tracer values in terms of land use between the NFBR and SFBR. All four tracers in the initial pool for the NFBR displayed an ability to discriminate; therefore, all four were used in the subsequent step in the selection process. In order to select the most effective composite fingerprint from this pool, multivariate discriminant function analysis was used and the results are shown in Table 2.3. These results indicated that three of the four tracers (^{15}N, ^{13}C, and TC) from the initial pool were capable of accurate classification of 95% of the source samples (number of observations =73). Discriminant analysis results of the SFBR tracer comparison study are shown in Table 2.4 and highlight the ability of the suite to work in a similar watershed. In the SFBR, all four tracers (^{15}N, ^{13}C, TN, and TC) were selected and were able to classify 98% of the samples correctly. Sources listed in the tables are in the order that they were selected, from most effective to least effective in terms of discrimination.

Delta ^{15}N and ^{13}C values were found to be highest in pastures, followed by banks and then subsurface throughout the NFBR and SFBR as shown in Table 2.1 and 2.2. This is likely due to preference for lighter isotopes during biogeochemical cycling. In pastures, plant preference for the lighter isotope causes enrichment in the heavier isotope when that plant is harvested (or consumed) and the lighter isotope removed from the system. Also, nitrification favors ^{14}N which leaves fields which have been fertilized with ammonium enriched in ^{15}N (Fox and Papanicolaou, 2008). Karamanous and Rennie (1980) showed that denitirification favors ^{14}N and can lead to ^{15}N enrichment. This explains higher ^{15}N values in the banks which are often anaerobic. It has been observed that enrichment tends to increase with depth (examined in these studies up to 60 cm) in the profile for both ^{15}N and ^{13}C (Hobbie et al, 1999, Trumbore, 2000, Amundson et al., 2003). This is thought to be primarily due to the age of soil organic matter with enrichment increasing with age. However, this phenomenon requires organic matter and nutrient cycling. Van Groenigen et al. (2005) studied ^{15}N and ^{18}O concentrations in soil N_2O gas and found that in all but two sub soils samples, ^{15}N values were lower than the topsoil.

The subsoils we sampled exhibited lower enrichment in ^{15}N. This is most likely due to the lack of organic matter inputs and a general lack of biotic activity in these piedmont subsoils reducing nutrient cycling and therefore preventing heavily enriched soils. Total Carbon values were found to follow the same pattern of highest values for pastures, followed by banks and then subsurface soils. This was probably due to pastures having the most organic inputs followed by banks and then subsurface soils.

To compare using automated samplers for suspended sediment collection to our previous, significantly more expensive, technique of utilizing a mobile continuous flow centrifuge, we used both methods at two sites (the outlet of the main stem and the Tom's Creek tributary) and compared them using ANOVA, the results of which are shown in Table 2.5. The sampling method employed at each site for each event is listed in Table 2.6. The two methods exhibited significant differences for the isotopic tracers but not for TC. However, it is worth noting that while we experienced a statistical difference between sampling methods, the differences in results were small (typically within 5-10%) when compared to the cost differences associated with the two (discussed in detail later). The cause of this discrepancy may lie in the fact that isotopic fractionation discriminated against the heavy isotope during evaporation. Sediment samples collected via centrifuge were oven-dried in beakers. Samples collected via ISCO samplers were collected on filters and oven dried. Both were dried overnight at 60^{o} C, however, the filtered samples had a greater surface area exposed during evaporation possibly explaining their higher enrichment values. Also, there may be an effect coming from the fact that the filter papers remove sediment down to 0.45 microns and the centrifuge may not extract particles down to the 0.45 μm range. Further testing is needed both on the particle size the centrifuge is capable of recovering and on the differences in fractionation during evaporation using both methods. Finally, the samples being compared are not subsets of one sample but rather individual samples, many from different events. It may be some of the differences are due to natural variations. In any case, freeze drying may be an alternative method of drying that would not change the isotopic ratio.

Figure 2.2 shows the mean turbidity values in nephelometric turbidity units (NTU) during events that we sampled from each site. Our previous study indicated an approximately one to one relationship between turbidity and suspended sediment concentration (Mukundan et al., 2010). The values ranged from 221 to 466 NTU with Tom's Creek exhibiting the highest values. It is likely that the Tom's Creek values are more in line with the rest of the points sampled, however, the stream level in one event sampled at Tom's reached bank full level and turbidity values were correspondingly high. Figures 2.3 and 2.4 illustrate individual sample source proportions using the deterministic solution to the mixing model from each site. All sites except Davis Creek (where only one event was sampled) display a dominance of bank sediment as a source. Figure 2.5 compares sediment contributions from each site at which we sampled using both deterministic (mean tracer value for sources and suspended sediment) and stochastic (using Monte Carlo simulations) approaches Although a different tracer suite was used in this study (^{15}N, ^{13}C, TC), results from the outlet of the main stem of the NFBR are similar to the results of our previous study (using ^{137}Cs and ^{15}N) where we sampled from this location when looking at sediment samples taken using the same method (centrifuge). Current results were 68% bank, 24% exposed subsoil, and 8% pasture. Previous results were 60% bank, 23% exposed subsoil, and 13% pasture. This confirms our previous results with a tracer suite which is both cheaper and requires less mass.

The mean values from the Monte Carlo simulations (stochastic method) were close to the values the model produced using mean tracer values (deterministic method). However, the box and whisker plots of the Monte Carlo results provide more information in terms of variability of the distributions and the associated uncertainty in the model results. Observing the distance between the first and third quartiles allows for an appreciation of the variability which may exist in the model results. At all of the sites, the range between the first and third quartiles for any given source was between 10 and 20%, except Tom's Creek where the results from automated sampling varied by as much 38 percent for the bank source. This information allowed us to see variability in possible contributions that a deterministic approach would not have disclosed.

Within the NFBR, there was a striking similarity in source origin in terms of the spatial distributions. From the outlet to the middle of the main stem and from the tributaries we sampled, the suspended sediment was predominantly of bank origin. This seemed to indicate that at least in this watershed (which we consider typical of the Southern Piedmont), regardless of variations in land use and stream order, the legacy sediments comprising the banks and floodplains and the geomorphologic processes which are occurring as the stream channels evolve toward a stable stage should be considered the primary factor in impairment for suspended sediment. Furthermore, considering the nature of the problem now defined, it is inherently difficult to prevent or even mitigate such a problem at this scale. Identifying bank areas of particular concern is possible but they will likely be numerous and expensive to restore. Time may be an important aspect of the solution as channels move towards equilibrium in terms of sediment.

While similarities in the spatial distribution of sediment sources existed, there were also dissimilarities. The main tributaries (Clarke's Creek and Tom's Creek) showed an increase in bank sediment relative to the main stem when looking at results from centrifuged samples using the deterministic approach. This may be due to one of several reasons. Referring to Simons model (Klimetz and Simon, 2007), the RGAs (Table 2.7) performed on the NFBR show a main stem which is predominantly at stage five, a stage where aggradation has begun and which directly precedes stage six or a stage of renewed equilibrium. However, many of the tributary reaches surveyed (Clarke's Creek was an exception) were at stage three or four suggesting that while the main stem may have begun to stabilize, the tributaries might still be generating sediment due to degradation and channel widening. In the early 1900's the lower section of the NFBR main stem was channelized under a program initiated by a Georgia drainage law passed in 1911 (Barrows and Phillips, 1917). This disturbance may have created a "nick point" of disturbance that has moved up from the lower main stem into the tributaries (Simon and Hupp, 1986). Also, there is the issue of field gullies in floodplains which we observed in the tributaries. These gullies are comprised of the same legacy sediments as the banks and are likely indistinguishable from a tracer perspective (we did not sample the gullies as an erosion source). We believe it may be possible that the elevated levels of bank sediments could at least in part be originating from the headcuts of these gullies. More investigation is needed in that regard.

However, these results become somewhat less clear when we begin to compare sampling methods and deterministic vs stochastic approaches to solving the mixing model. Comparing Tom's Creek and the NFBR in terms of automated samples shows only a modest increase in banks for Tom's relative to the NFBR with respect to deterministic solutions and in fact a decrease in banks relative to the NFBR with respect to the mean of the stochastic solutions.

Observing all three in terms of centrifuged sampling methods and stochastic solutions shows Clarke's Creek to have the lowest percentage of bank contributions. This may be due to the fact that Clarke's Creek had a channel stage which was predominantly stage 5, the same as the main stem.

There were dissimilarities between the two main sub-basins as well. Tom's Creek exhibited less sediment of subsurface origin than Clarke's Creek. Of the two, which are both quite rural, Clarke's Creek appears to have a larger number of residences. Also, while both sub basins contain a number of unpaved roads and road ditches, Clarke's Creek has several which are on steep gradients and have large incised road ditches. Tom's Creek exhibited more sediment from bank origin. This was confirmed by RGA results which showed Tom's Creek was predominantly stage three, while Clarke's Creek was predominantly stage five. Also, both tributaries are home to several farm ponds and decades old sediment detention ponds and their effect on the results is unknown. While there were only two samples from Davis creek, it showed higher subsurface inputs than any of the other locations. It is unclear why this occurred, but it may be that the single event that was sampled was atypical. Only one event was sampled due to the tendency of the access point to flash flood.

Streamlined Approach

One of our objectives in this study was to modify the fingerprinting technique for use by state agencies, particularly agencies in the Southern Piedmont. Our purpose was to transform fingerprinting from a research tool to an operational tool adapted for our region (Walling, 2010). Traditional approaches to fingerprinting have been performed in the context of research and have not thought to examine the issues of cost or time. It was our intent to provide an outline of the steps necessary to conduct a fingerprinting study in the Southern Piedmont using the most cost effective means available.. The main benefit provided comes from the reduced costs associated with having the tracer selection process abbreviated and using a tracer suite which is suitable for automated samplers. Table 2.8 compares costs of the two studies we have completed. The costs for the previous approach are much higher due to the need for a modified mobile centrifuge (modifications included conversion from electric to gas power, custom frame, pump, and new wiring and hoses) and the analysis costs associated with the tracer selection process. Using the latter method, costs were limited to an ISCO sampler and a single analysis. The following is an outline of that approach.

The first step in this streamlined approach is to determine contributing sub basins and their respective land uses using GIS. This can be done with the USEPA free BASINS (Better Assessment Science Integrating point and Non-point Sources) software (USEPA, 2011c). This software contains data for all watersheds in the U.S. and can be used for sub basin delineations and land use characteristics. Online tutorials are available on the EPA BASINS website.

The second step is to characterize the stream channels utilizing RGAs or some other stream classification system such as the Rosgen system (Rosgen, 1985, 1994). Land use data alone does not provide a complete picture in terms of potential sediment sources. RGAs are quickly and inexpensively performed (with training) and the stream stability index provides an effective method to compare streams in terms of bank erosion potential.

The third step is sampling. Using the methods outlined above, source sampling can be accomplished in a matter of days, providing there is ample access in the areas of interest. Sample sizes should be 10 or more per source to ensure statistical power and an accurate representation of sources. Bank sampling can be performed alongside RGA. Stream sampling is easily performed using automated samplers. The use of ISCO or other samplers equipped with pressure transducers or flow meters allows not only for automated composite samples during stormflow, but also for the collection of flow data on ungauged streams, provided a discharge-gauge relationship is developed. If automated samplers are found to be too expensive, an even less costly method exists. Time integrated samplers (Phillips et al., 2000) consist of in situ sedimentation chambers made of commercially available polyvinylchloride (PVC). Small diameter inlet and outlet tubes allow water to enter the chamber where it loses much of its velocity and allows for sedimentation. Samplers are placed horizontally in the stream channel and secured to metal posts. After an event they are removed and a single sample representing the entire event is collected. Individual samplers can be constructed for < $20.   Sample preparation and analysis should consist of air-drying and sieving source samples to 2 mm followed by particle size analysis. Source samples need to be ball milled for isotope mass spectrometry. Suspended sediment samples should be poured through a -0.05-mm sieve to remove sand and vacuum-filtered through a 0.45-micron filter for suspended sediment removal. Oven-drying and grinding using a mortar and pestle are all that is need for sample preparation.

While automated sample collection has a number of advantages, several pitfalls should be considered. First, while we were able to composite samples by hydrograph position (generally consisting of two to six samples) using ISCO samplers, each individual sample represents only one liter of water collected. Using a technique such as the centrifuge allows for hundreds of liters of water to be collected and each sample therefore represents a better temporal integration. Also, our results indicated a small but statistically significant difference in isotopic values which we expect was caused by isotopic discrimination during evaporation. Freeze drying of collected sediment might eliminate further fractionation and again we would suggest its use.

Tracer selection is the next step. We have found that the tracer suite we used could distinguish three sources in the NFBR and in a similar watershed nearby. The Kruskall Wallis *H*-test and discriminant function analysis indicated that they could distinguish between at least three sources. The mixture of elemental and isotopic tracers provides enough variety to insure a robust tracer suite. Furthermore, only one analysis (mass spectrometry) is required for all tracers. Mass spectrometry is available at numerous labs around the U.S. with turnaround times under a month. In contrast, radioisotope analysis is available at only a few labs. The mass necessary is small enough that sediment collected on filter papers is adequate and the analysis is quite inexpensive (<$15 per sample as compared to >$100 for radioisotopes). Any statistical package capable of performing the operations discussed above would be adequate for the tracer selection process.

Finally, mixing model analysis can be performed using Microsoft Excel using the free Solver plug-in software. If uncertainty analysis is desired, Palisades @RISK is an option but any software capable of performing Monte Carlo simulations with the mixing model would suffice. Results using uncertainty analysis should be desirable for agencies making decisions about how to implement TMDLs and BMPs. If there is a high degree of uncertainty regarding which are the main sources, then further analysis should be undertaken before implementing changes.

Using this process and the numerous studies which have been discussed both here and in the literature, it should be possible to use sediment fingerprinting as an operational tool in TMDL planning and implementation.

Conclusions

The sub-basins observed in this study showed that bank erosion was a dominant process throughout this watershed. While variations existed and were perhaps the result of slight differences in land use and stream channel stage, overall we found that the results were very similar both from the middle and outlet of the main stem and from several tributaries. One of the questions we asked following the previous study was whether or not a single sample location at the outlet of the watershed was providing us with an accurate picture of sediment origin. It was possible that perhaps only the local area of the basin was contributing a majority of bank derived sediment, skewing our results. Now it seems that bank erosion is common throughout the entire system and that channel processes coupled with legacy sediments dominate sediment generation. The results of this study show the applicability of the fingerprinting technique as an operational tool in TMDL implementation and the possibility of a cost-saving regional tracer suite. Used in combination with RGAs, an accurate picture of sediment origin in watersheds can be established.

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Table 2.1. NFBR mean tracer values, coefficients of variation (CV), results of Kruskal-Wallis H-test, and distributions expressed in terms of the fine fraction (silt and clay).

Tracer	Bank	Pasture	Subsurface	*H* value	*P* value
$\delta^{15}N$(‰)	5.75	8.35	0.85	58.94	< 0.0001
SE	1.22	2.33	1.39		
CV (%)	21.30	27.87	162.31		
Distribution	Beta General	Logistic	Beta General		
$\delta^{13}C$ (‰)	-25.72	-23.19	-24.44	39.56	< 0.0001
SE	0.82	1.88	1.31		
CV (%)	3.19	8.11	5.36		
Distribution	Log Logistic	Weibull	Log Normal		
TC (%)	2.24	17.57	1.37	61.62	< 0.0001
SE	1.01	10.30	1.05		
CV (%)	45.05	58.60	76.50		
Distribution	Beta General	Beta General	Beta General		
TN (%)	0.34	0.79	0.64	16.6	0.0002
SE	0.38	0.67	0.44		
CV (%)	113.55	85.66	68.62		
Distribution	Log Logistic	Gamma	Pearson 5		

Table 2.2. SFBR mean tracer values, coefficients of variation (CV), and results of Kruskall-Wallis H-test expressed in terms of the fine fraction (silt and clay).

Tracer	Bank	Pasture	Subsurface	*H* value	*P* value
$\delta\ ^{15}N$(‰)	3.99	6.28	0.76	28.417	< 0.0001
SE	1.04	2.73	1.65		
CV (%)	25.97	43.48	216.48		
$\delta\ ^{13}C$ (‰)	-27.80	-22.01	-24.49	28.816	< 0.0001
SE	1.70	2.30	1.31		
CV (%)	6.12	10.46	5.34		
TC (%)	1.27	6.12	0.35	32.3882	< 0.0001
SE	0.38	2.47	0.20		
CV (%)	29.96	40.36	57.72		
TN (%)	0.08	0.52	0.02	31.315	<0.0001
SE	0.03	0.22	0.01		
CV (%)	32.34	41.03	53.29		

Table 2.3. Stepwise discriminant function analysis (DA) used in the tracer suite selection process.

No. of variables	Variables	Partial R^2	F	Pr > F	Wilks' Lambda	Pr < Lambda	Samples Correctly Classified %
1	^{15}N	0.817	158.988	< 0.0001	0.183	< 0.0001	90
2	^{15}N, ^{13}C	0.549	42.625	< 0.0001	0.082	< 0.0001	92
3	^{15}N, ^{13}C, and TC	0.428	25.848	< 0.0001	0.047	< 0.0001	95

Table 2.4. Stepwise discriminant function analysis results from the South Fork Broad River.

No. of variables	Variables	Partial R^2	F	Pr > F	Wilks' Lambda	Pr < Lambda	Samples Correctly Classified %
1	^{15}N	0.734	31.255	< 0.0001	0.266	< 0.0001	66
2	TN / ^{15}N	0.706	26.461	< 0.0001	0.078	< 0.0001	89
3	TN / ^{15}N / ^{13}C	0.622	17.526	< 0.0001	0.030	< 0.0001	98
4	TN / ^{15}N / TC / ^{13}C	0.393	6.693	0.001	0.018	< 0.0001	98

Table 2.5. ANOVA comparison of sampling methods employed.

Site	Method	n samples	Mean δ 15N(‰)	Mean δ 13C (‰)	Mean TC(%)	Mean TN (%)
Main Stem	Centrifuge	11	4.642**	-27.042**	3.458	0.276
Main Stem	ISCO	14	6.584	-25.609	3.219	0.309
Tom's Creek	Centrifuge	13	6.384**	-26.262**	3.452	0.243
Tom's Creek	ISCO	9	8.523	-25.169	3.521	0.343

****** Centrifuge and ISCO differences statistically significant at the *P* = 0.01 level.

Table 2.6. Event number, site, sampling method, number of samples collected, date, rainfall, and average turbidity of samples collect during the study.

Event Number	Site	Sampling Method	Number of Samples	Date	Rainfall mm	Turbidity (NTU)
1	Tom's Creek	Centrifuge	4	9/21/2009	88.4	157
2	Clarke's Creek	Centrifuge	1	10/12/2009	40.9	203
3	Clarke's Creek	Centrifuge	1	10/14/2009	25.4	65
4	Tom's Creek	Centrifuge	2	12/9/2009	57.7	460
4	Clarke's Creek	Centrifuge	1	12/9/2009	57.7	358
5	Clarke's Creek	Centrifuge	1	1/21/2010	26.4	235
6	Tom's Creek	Centrifuge	4	1/24/2010	69.3	972
7	Clarke's Creek	Centrifuge	2	2/5/2010	63.2	217
8	Outlet Main Stem	Centrifuge	3	5/3/2010	40.9	228
9	Tom's Creek	Centrifuge	3	11/30/2010	63.8	654
9	Outlet Main Stem	Centrifuge	3	12/1/2010	63.8	273
10	Outlet Main Stem	Centrifuge	2	12/4/2010	6.4	285
11	Outlet Main Stem	Centrifuge	1	2/2/2011	30.7	140
11	Outlet Main Stem	ISCO	3	2/2/2011	30.7	420
11	Tom's Creek	ISCO	3	2/2/2011	30.7	532
11	Middle Main Stem	ISCO	3	2/2/2011	30.7	385
12	Tom's Creek	ISCO	2	2/5/2011	38.1	159
13	Tom's Creek	ISCO	2	3/6/2011	49.3	293
13	Outlet Main Stem	ISCO	1	3/6/2011	49.3	168
14	Clarke's Creek	Centrifuge	1	3/9/2011	34.0	333
14	Outlet Main Stem	ISCO	3	3/10/2011	34.0	298
14	Outlet Main Stem	Centrifuge	4	3/10/2011	34.0	218
14	Middle Main Stem	ISCO	4	3/10/2011	34.0	291
14	Tom's Creek	ISCO	2	3/11/2011	34.0	414
15	Outlet Main Stem	ISCO	3	3/15/2011	21.8	496

Table 2.7. Mean stability index value and predominant stage of channel evolution for streams in the NFBR.

Stream	Mean Index Value	Predominant Stage
NFBR main stem	17.75	5
Tom's Creek	17.62	3
Clarke's Creek	17.19	5
Davis Creek	18.8	4

Table 2.8. Cost comparison of our previous method vs the streamlined approach.

Item	Unit Cost	Number	Previous Approach	Streamlined Approach
Centrifuge, Pump, and Modifications	$18,000	1	$18,000	0
ISCO sampler and equipment	$5,950	1	0	$5950
Radioisotope analysis	$100	200	$20,000	0
ICP analysis	$15	200	$3,000	0
Total C,N,P,and S	$20	200	$4,000	0
Isotope Mass Spec analysis	$8	200	$1,600	$1,600
		Total	$46,600	$7,550

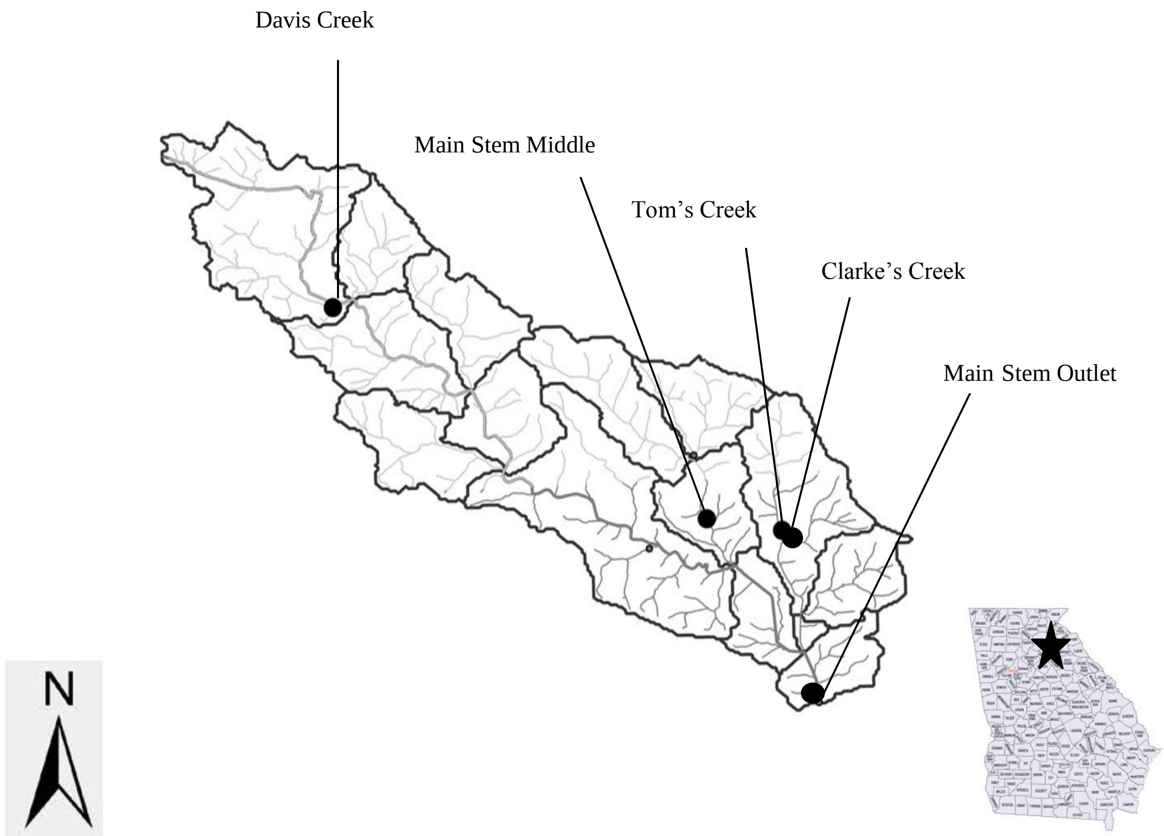

Figure 2.1. Suspended sediment sampling locations in the NFBR

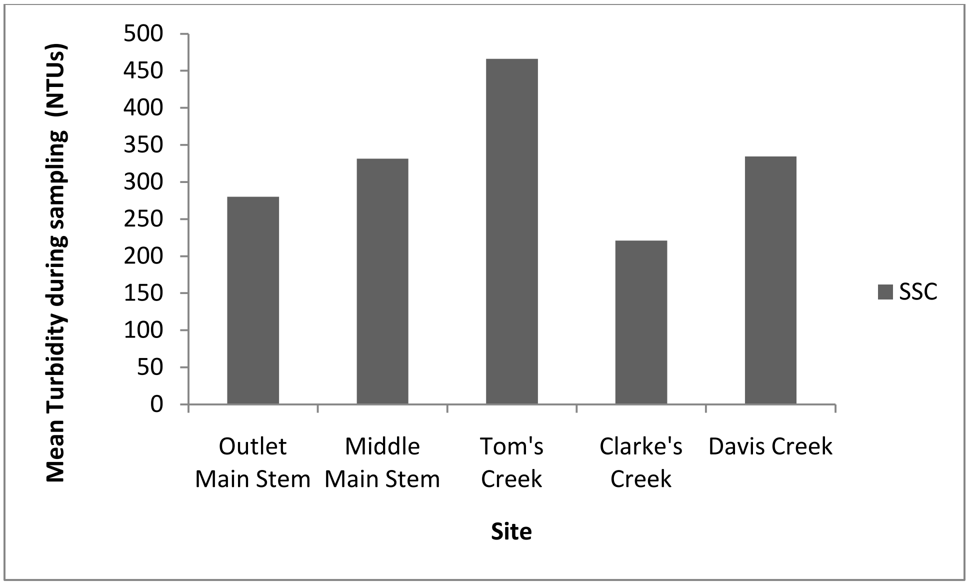

Figure 2.2 Mean turbidity values during sampled events at stream sampling sites.

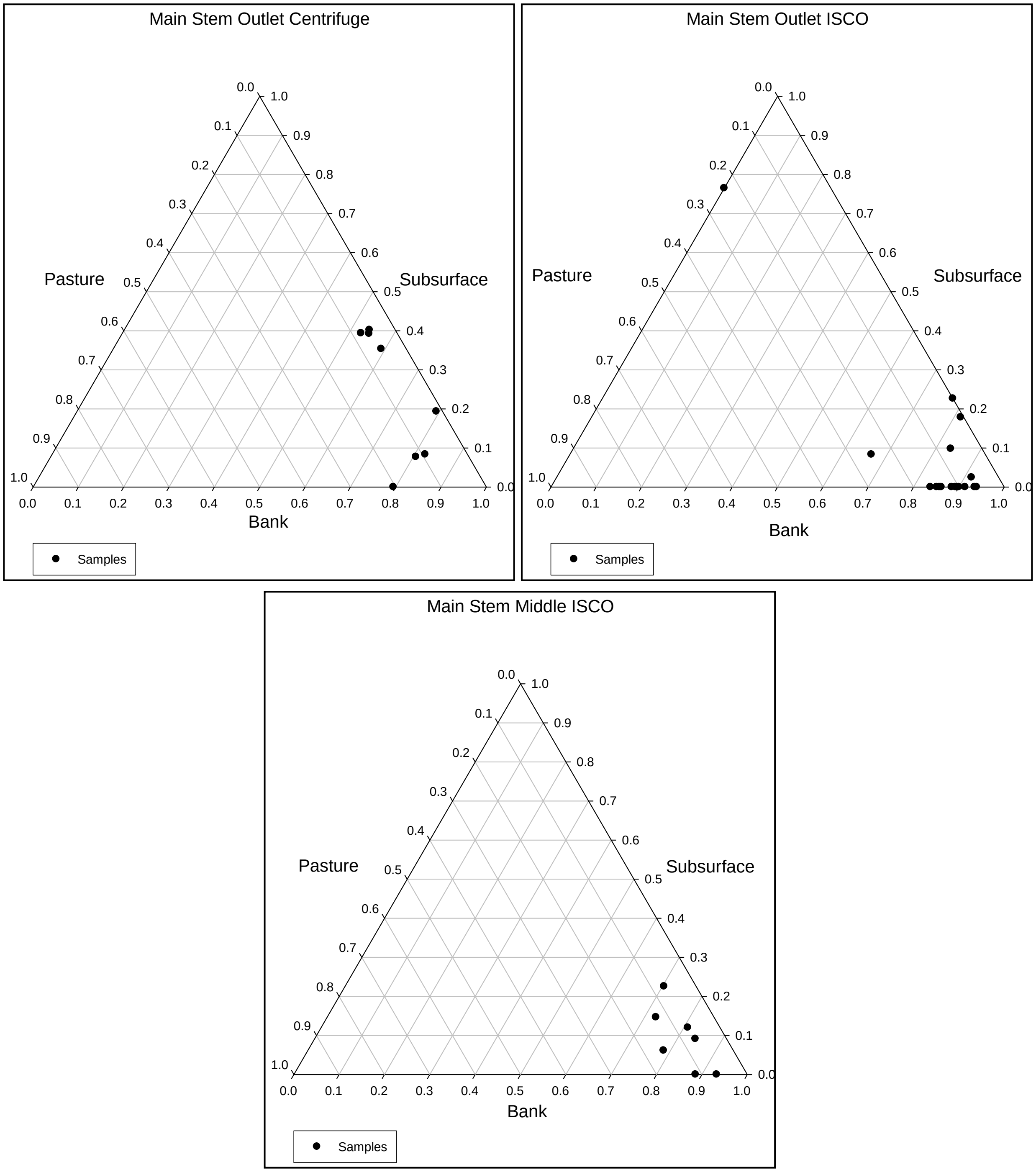

Fig 2.3. Individual samples values for NFBR main stem.

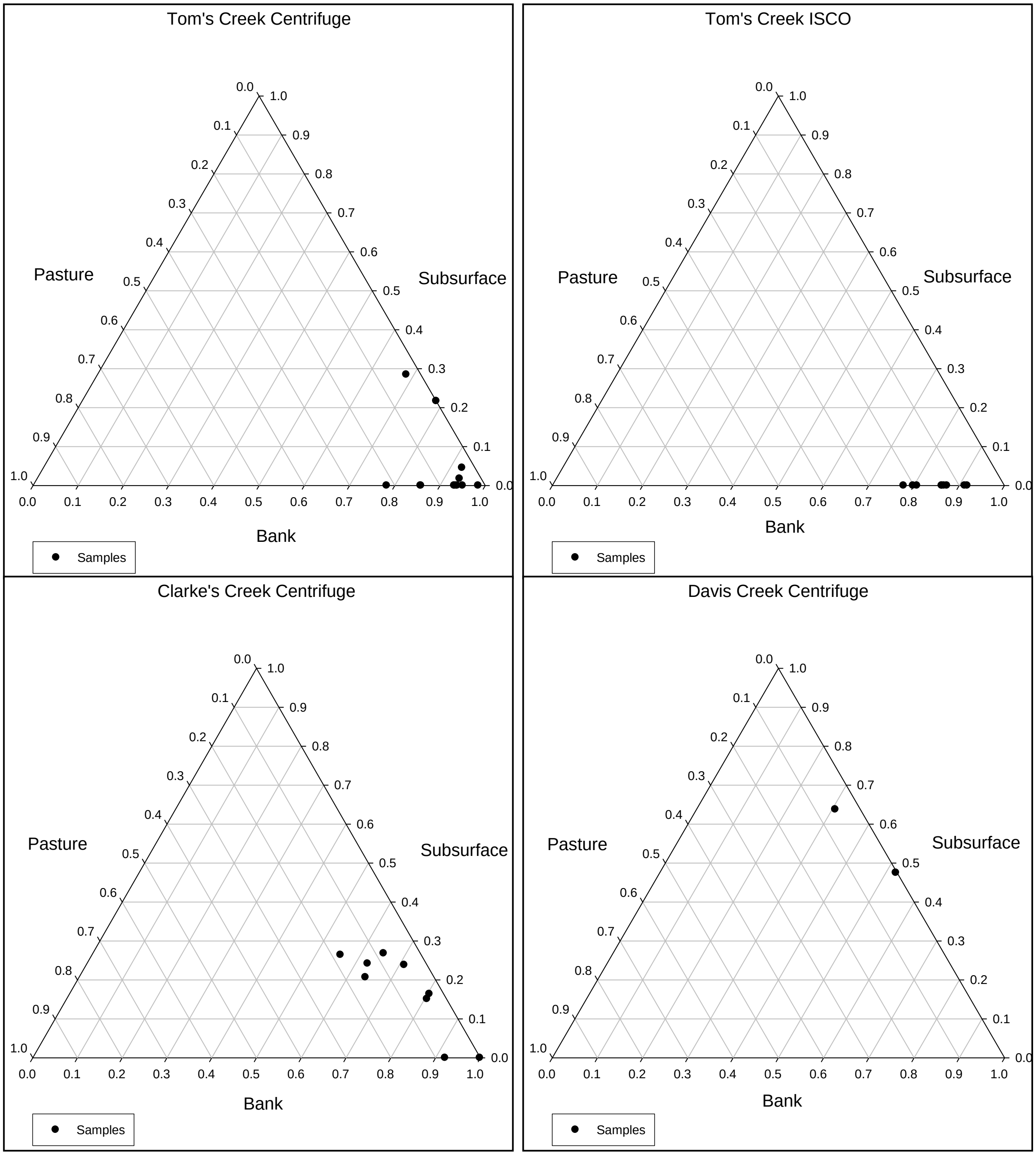

Figure 2.4. Individual sample values for tributaries of the NFBR.

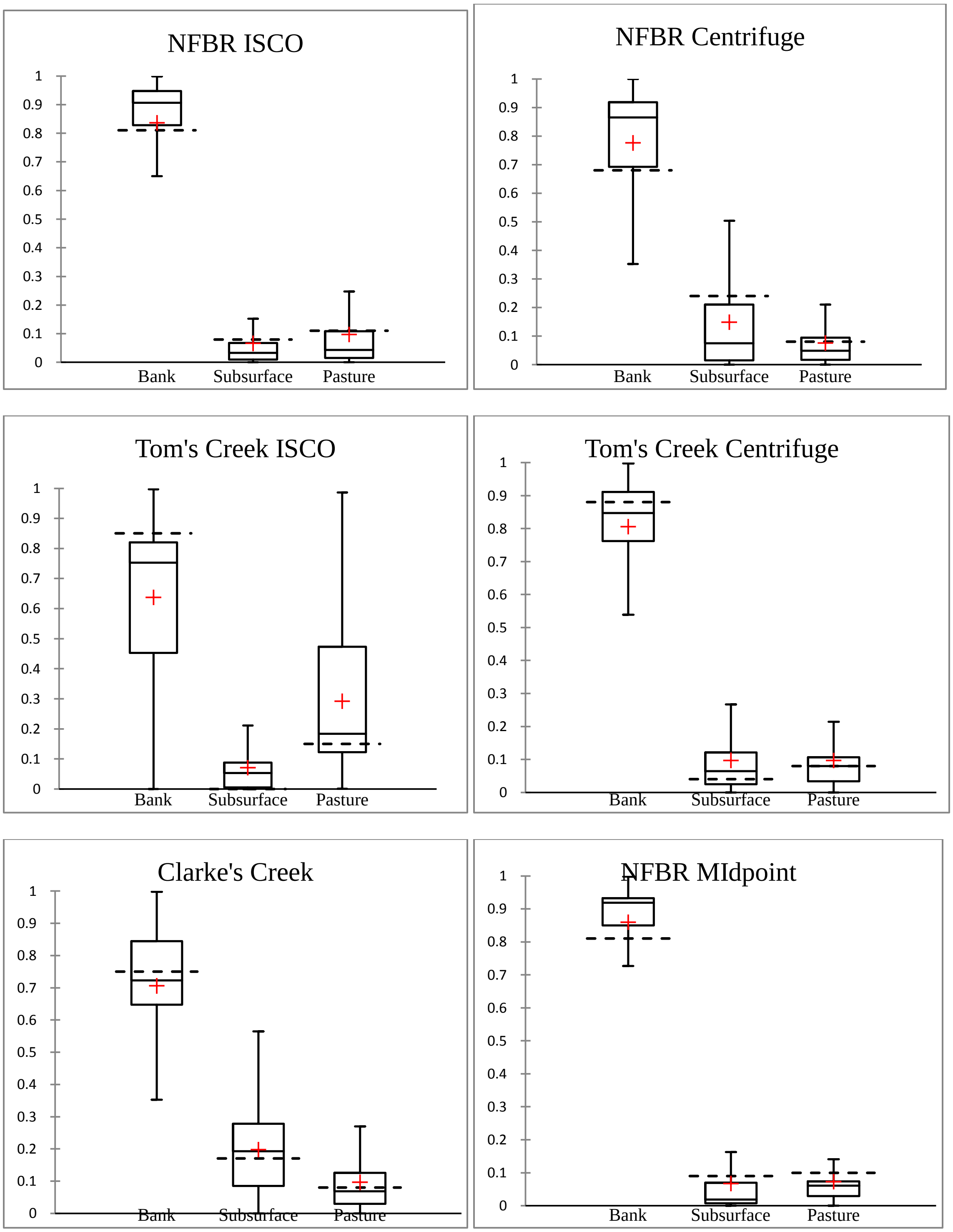

Figure 2.5. Mixing Model results. Whisker plots (plus mark represents mean from simulations) are from Monte Carlo simulations and the dashed line indicates the value from using just the tracer mean in the mixing model.