

# **ABSTRACT**

Title of Document:                   QUANTIFYING FINE SEDIMENT  
  SOURCES IN THE NORTHEAST BRANCH  
  OF THE ANACOSTIA RIVER,  
  MARYLAND, USING TRACE ELEMENTS  
  AND RADIONUCLIDES

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Fine sediment sources were characterized in an urban watershed, the Northeast Branch of the Anacostia River, which drains to the Chesapeake Bay. Concentrations of 63 elements and two radionuclides were measured in possible sediment sources and suspended sediment collected at the watershed outlet during storm events. Methodology for selecting tracers was developed so the sediment fingerprinting method could effectively determine the relative quantity of sediment contributed by each source to the suspended fraction. The amount of enrichment of trace elements in sediment sources and suspended sediment was determined by calculating enrichment ratios, which are ratios of the normalized concentration of elements in the sample relative to their average normalized concentration in the Earth's upper continental crust. Streambanks contributed the highest relative quantity of sediment in the fall and spring while upland areas contributed mostly during winter. Street residue contributed 12% on average and was the source most concentrated in anthropogenically enriched elements.

QUANTIFYING FINE SEDIMENT SOURCES  
IN THE NORTHEAST BRANCH OF THE ANACOSTIA RIVER  
USING TRACE ELEMENTS AND RADIONUCLIDES

By

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## Dedication

To acknowledge their patience and confidence in me, this work is dedicated to my husband Erik Devereux and children Alexander Devereux and Mildred Devereux.

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# Chapter 1: Introduction

## Problem

Sediment is defined as particles derived from rocks and soils that are transported and deposited (USGS, 2004). Organic material is also included in the transport process (SSSA, 2006). In urban areas, sediment may be derived from natural hillslopes, yards in residential areas, floodplains, stream banks, stream beds, and from residue that accumulates on roads. Particulate matter may also be atmospherically deposited within the watershed. The transport process requires that sediment first become mobilized through water or wind erosion, and then transported from its source. Although significant amounts of transported sediment are stored within a river system, some of this sediment, particularly the fine-grained fraction, travels downstream to bays and oceans.

Sediment is the leading water pollutant in the United States (Woodward and Foster, 1997). The U.S. EPA has regulated sediment in waterways by establishing Total Maximum Daily Loads (TMDL). Suspended sediment diminishes light penetration in water, which affects submerged aquatic vegetation, and affects habitat for benthic biota such as blue crabs and rockfish. The health and extent of sub-aquatic vegetation is used as an indicator of the level of impairment caused by fine sediment in water bodies. The loss of aquatic life has a direct economic impact, particularly when it affects fisheries and the service industries that depend on seafood production.

In addition to ecosystem problems caused by light attenuation due to suspended sediment in the water column, fine-grained sediment transport can also affect the concentration and distribution of sediment-bound contaminants. Some of the most common contaminants that adhere to sediment include heavy metals, nutrients (particularly P and K), and organic substances. For example, 57% of streams sampled in the U.S. exceed the EPA total phosphorus standards (U.S. Geological Survey, 1999).

Knowledge of sediment sources is essential in efforts to restore sediment-impaired watersheds. This is important for two reasons: 1) identification of sediment sources is the first step in reducing sediment pollution in water bodies, and 2) sediment characteristics (oxyhydroxide coatings, organic matter content, etc.) develop in situ in the landscape; these characteristics in turn influence chemical and physical properties (Marvin et al., 2004). These properties affect the type and amount of contaminants that may adsorb to sediments. In addition, sediment loss is not equally distributed in the landscape. Knowledge of sediment sources and their relation to geology and soil characteristics would be a significant step for science-based management practices to be targeted to zones at high risk for sediment loss.

## Background

A sediment budget for a watershed consists of measurements of sediment input, sediment storage, and sediment output from the watershed. Sediment input into the watershed results from hillslope and channel erosion. Erosion measurements give a direct measurement of the contribution of sediment from that source to the sediment budget. For example, direct measurements of channel bank erosion are made by examining changes over time in channels using aerial photography, erosion pins, and sequential surveys of streams (Dunne and Leopold, 1978). Erosion measurements give a direct measurement of erosion rates from specific sources, but in most watersheds, significant amounts of the sediment will be stored within the basin. Thus, sediment erosion measurements can not be used to directly measure the sources of sediment that is exported from the basin.

Sediment transport and storage in a watershed can be determined by direct measurements of suspended sediment load within a watershed system. The sediment load is measured at various places in a stream network, and sources are estimated from the various loads. However, extensive sediment monitoring networks are required to determine sediment loads, losses due to storage, and relationship between sediment loads and sediment sources. Detailed sediment budgets require measurements of both erosion from sources and transport of sediment within watersheds. This method is expensive and time-consuming (Dunne and Leopold, 1978).

Sediment fingerprinting is a method that was developed to determine the sources of the suspended fraction that is transported out of a watershed. This method compares sediment from a variety of different potential sources with suspended sediment collected at a downstream location. The method compares the amount of various tracers, which may be geochemical, mineralogical, or mineral magnetic, in various sediment sources to the suspended sediment. First developed in the 1970s, sediment fingerprinting determines sediment sources by using physical or chemical properties (Collins et al., 1997a; Walling and Woodward, 1992; de Boer and Crosby, 1995; Wallbrink et al., 1998; Walling et al., 1999; Rowan et al., 2000; Owens et al., 2000; Jansson 2002; Gruszowski et al., 2003; Jenkins et al., 2002; Motha et al., 2003; Papinicolaou et al., 2003; Motha et al., 2003; Rhoton et al., 2005; Walling, 2005; Carter et al., 2003; Gellis and Landwehr, 2006).

Sediment source identification and quantification techniques have advanced substantially in the past five years. The use of the various tracers would not be possible if the tracer characteristics change through the erosion process (Motha et al., 2002; Gao et al., 2005). Previously, researchers investigated the best way to use radionuclides as a characteristic of fingerprints (Wallbrink et al., 1998; Nagle and Ritchie, 2004). Using stable or radiogenic isotopes as part of a fingerprint has also been researched (Papinicolaou et al., 2003). Determining the effects of particle size has been thoroughly explored by a variety of authors (Motha et al., 2003; Marvin et al., 2004). While fingerprinting originally differentiated sources by land use, the

impact of erosion of roads in rural areas has also been investigated (Gruszowski et al., 2003). Clays also have been used as a component in fingerprints with success (Deboer and Crosby, 1995). The sediment fingerprinting method has become accepted as a valid method for identifying sediment sources (Walling, 2005).

Sediment fingerprinting has not been used widely in watersheds with urban areas (Carter et al., 2003). The tracers that are commonly used in sediment fingerprinting research may not be effective in urban areas (Jeelani and Shah, 2006, Leung and Jiao, 2006). Urban areas likely have a stronger anthropogenic component than rural or forested areas, resulting in a different chemical fingerprint. In addition, urbanization may decrease sediment storage areas because buildings are constructed on floodplains – resulting in impervious surfaces at just those locations where sediment could be stored as part of natural stream processes (Jacobson and Coleman, 1986). Also, impervious surface areas, such as parking lots, buildings, and concrete or asphalt roads, are not erodible so the areas that are sediment sources are necessarily different than those in rural or forested watersheds.

### Objectives

The purpose of this research is to extend the sediment fingerprinting methodology to discriminate and quantify sediment sources in an urban watershed. In comparing the sources of sediment to suspended sediment, sources are grouped by subwatershed and also by landscape position. An adapted mixing model (Gellis and Landwehr, 2006) is used to determine the relative quantity of sediment derived from various sources.

Testing the applicability of sediment fingerprinting methodology in urban areas is important for several reasons. Developed land is increasing at a rapid rate in many parts of the world. In the Washington, DC area, developed land increased 64% from 2,544 to 4,167 km<sup>2</sup> between 1986 and 2000 (Jantz et al., 2005). Legislation requiring water quality improvement has been used as the basis for establishing total maximum daily load (TMDL) requirements for sediment. There is a sediment TMDL established for the Anacostia River (U.S. EPA, 2006). Decisions on how best to manage and improve watersheds with sediment-impaired water require information about the sources of sediment.

### Description of Study Area

The Chesapeake Bay watershed encompasses 168,000 km<sup>2</sup> and includes parts of the states of New York, Pennsylvania, West Virginia, Maryland, Delaware, Virginia and all of the District of Columbia. The Anacostia River drains northern Washington D.C. and adjacent portions of Maryland to the Chesapeake Bay. The study area is the Northeast Branch of the Anacostia River watershed, which is northeast of Washington, D.C. in Maryland. The drainage area of the Northeast Branch watershed is 188.5 km<sup>2</sup>.

Presently the Anacostia River watershed, which includes the Northeast Branch watershed, is 64% urban, 27% forested, 8% agricultural, <½ % wetlands, and <½ % other categories (Fig 1-1) (Maryland Department of Natural Resources, 2000). Impervious land is 33% (Maryland Department of Natural Resources, 2000). The Northeast Branch area of the Anacostia is the oldest developed portion of the watershed, developed primarily in the time period between 1960 and 1970 (Jacobson and Coleman, 1986). While construction projects are currently taking place, there are no current wide-spread Earth-moving projects.

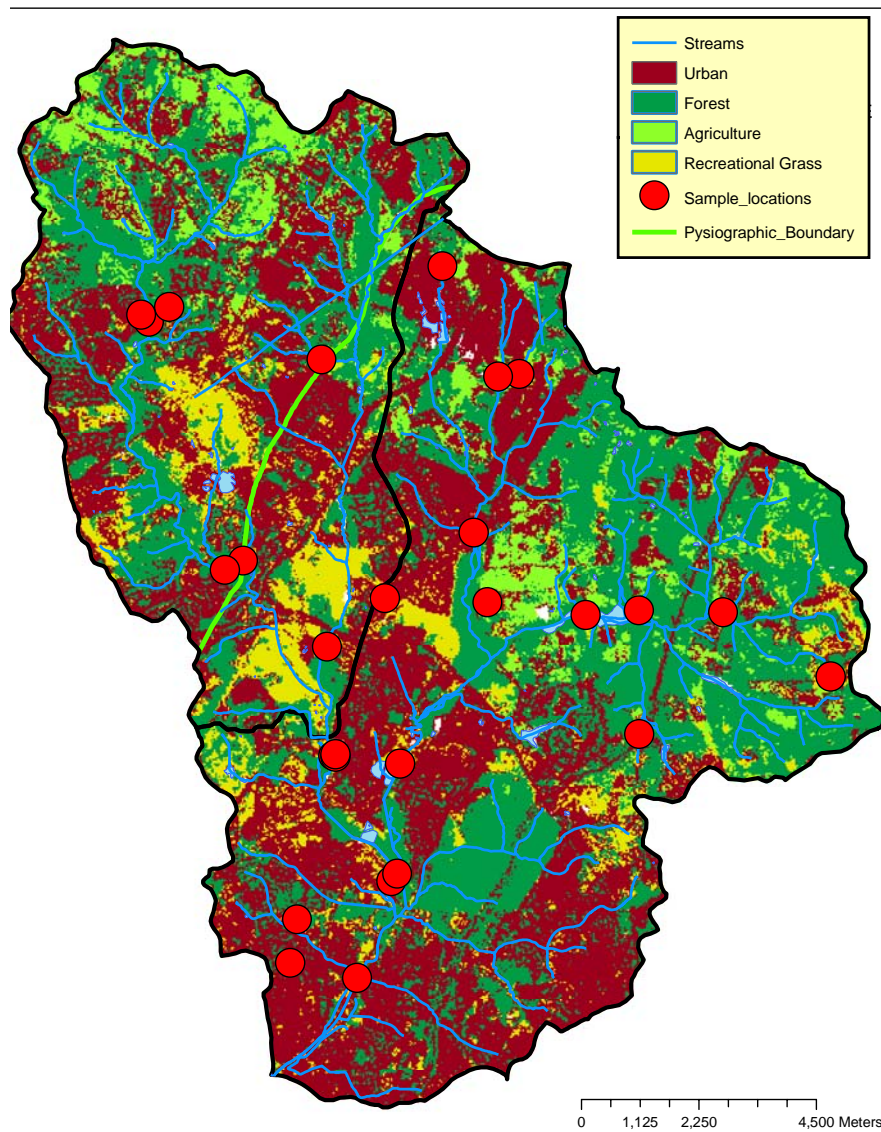


Fig: 1-1 Land Use of Study Site. Note that recreational grasses are ball fields.

The Northeast Branch watershed spans two physiographic regions – the Piedmont and the Coastal Plain. The physiographic province reflects the geology and topography. Coastal Plain geology primarily comprises silt-clay facies of the Potomac Group (Patuxent Formation), which is Early Cretaceous in age. The Potomac Group is

fluvially deposited quartz, with some sandstone and chert. The Coastal Plain also includes Arundel Clay and much of the lower Patapsco Formation. The Coastal Plain in this area is highly-weathered Piedmont material from fluvial deposition. Upland deposits of the Coastal Plain are fluvial sediments of the ancestral Potomac River and are of the late Miocene and Pliocene periods. Terrace deposits are the product of stream erosion during the early Quaternary Period. These are primarily unconsolidated sediments. The Coastal Plain ranges in age from the Cretaceous to Quaternary periods (Markewich et al, 1987).

Mapped units in the Piedmont, including the Laurel formation, are characterized by Precambrian crystalline metamorphic rocks with occasional intrusions of igneous rocks. The granite, gneiss, schist, and other crystalline rocks range in age from Precambrian to late Paleozoic. Piedmont upland deposits are high in vermiculite clay (Cleaves et al., 1968; Hack, 1977; Glaser, 1996; Csato et al., 2006).

In addition to encompassing two physiographic regions, the Northeast Branch watershed is made up of two subwatersheds. The west subwatershed is influenced by the Piedmont geology and the east subwatershed is characterized by the Coastal Plain geology. The subwatershed boundary is mapped east of the physiographic boundary. In the west subwatershed the land use is urban—a combination of commercial and residential. There are numerous wooded parks along the streams. In the east subwatershed land use is industrial, commercial, residential, forested and agricultural. There are gravel pits along the headwaters of a stream in the east subwatershed. Exhausted gravel pits are used as dumps for yard waste and they are also sites for suburban development. Also located in the east subwatershed is rural land that has long been managed as farmland by USDA-ARS and a forested national park.

Four main tributaries make up the Northeast Branch watershed. From west to east they are: Paint Branch, Little Paint Branch, Indian Creek, and Beaverdam Creek. The Little Paint Branch drains to the Paint Branch. Beaverdam Creek drains to Indian Creek. The confluence of Paint Branch and Indian Creek form the Northeast Branch of the Anacostia. The Piedmont streams include the upstream reaches of the Paint Branch and Little Paint Branch and are gravel and boulder bedded. Some of the boulders range to several meters in diameter. The floodplains are small, between three and six meters in many locations. The region is hilly and slopes are high and steep. The soils are more fine-grained than those in the Coastal Plain. The downstream reaches of these streams are characterized by fewer boulders and more sand.

The Coastal Plain streams include the entirety of Indian Creek and Beaverdam Creek and the lower portions of Paint Branch and Little Paint Branch. The streams are sand, silt, and clay bottomed. Sand bars migrate through the two streams that originate in the Piedmont. The Coastal Plain is a low rolling plain. The Coastal Plain soils are sandier than those of the Piedmont.

The downstream portions of the streams are channelized with cement, gabions, or granite blocks. The channelization inhibits sediment storage and increases stream flow velocity by decreasing friction.

The climate is humid continental with an average temperature of 13.2 °C and an average annual rainfall of 117 cm (NOAA 2005). There are four distinct seasons with mild winters. Rainfall is evenly distributed throughout the year; storms with broad aerial extent occur primarily in winter months. There are isolated thunderstorms in the summer that deliver rain quickly and create flashy stream flow. These summer thunderstorms typically do not span the entire watershed.

#### Site Selection and Sediment Sampling

Sediment sources were assumed to be the following: upland (non-channel) sites, stream bank sites, and sediment on paved surfaces. Therefore, a sampling strategy was developed to sample these sites throughout the stream system and within both physiographic provinces. Sediment source sample locations were located along reaches of each of the four tributaries and the main stem to represent both physiographic regions, both subwatersheds, multiple landscape positions, and each land use in the Northeast Branch watershed. Samples were collected from upstream and downstream reaches of the streams. The objective was to collect sediment source samples so that they could be grouped to maximize variation between groups. It was not known beforehand which grouping would result in maximum variation between groups.

The high percentage of impervious surfaces necessitated more soil samples from banks because much of the upland area was paved. Of the bank samples, there were three sample sites along the Paint Branch, two along the Little Paint Branch, four along Indian Creek, five along Beaverdam, and three along the Northeast Branch. Bank sample sites were chosen where the stream width or depth changed, topography changed, there was a confluence, and/or significant erosion was visible. These geomorphic changes in the stream areas indicate a possible change in soils and sediments from the stream reaches above those areas. At five of these stream bank sites, samples were taken along a transect moving away from the bank to include the landscape positions of stream bank, floodplain, and upland. Depending on the topography, the upland position was either a backslope or a summit position. These five sites were selected to represent physiographic region and land use.

The watershed included many urban areas that could contribute sediment with significantly different chemical characteristics to the stream. Additional sediment inputs in this urban area include street residue, sewage, and atmospheric particulate matter. Street residue was collected for both physiographic regions in the urbanized portions of the watershed. One construction site located adjacent to the stream and very near the suspended sediment collection site was sampled as were four point bars. It was outside the scope of this project to collect sewage or atmospheric particulate

matter. However, atmospheric particulate matter data was available from other watersheds for comparison.

Suspended sediment samples were collected at the outlet of the Northeast Branch watershed. The sediment was collected during storm events by pumping stream water into three 208 liter plastic-lined barrels in the back of a pick-up truck. The samples were driven to a continuous centrifuge and the sediment was recovered. Suspended sediment sampling was collected in such a way as to maximize the amount of sediment collected. Enough sediment had to be available to perform the lab analysis necessary to measure the concentration of the various tracers. This is especially true for the radionuclide analysis where error decreases with increased sample mass.

The Northeast Branch watershed is a sediment-limited system with average turbidity of 11.8 and median turbidity of 2.9, as measured by U.S. Geological Survey from September 2005 to February 2006 using monochrome near infra-red LED light, 780-900 nm, detection angle 90 +/- 2.5 degrees. Maximum turbidity occurs during the rising limb of the hydrograph of storm events (Appendix E). Thus, sampling was targeted for the rising limb of the hydrograph for storm events that covered the entire 188 km<sup>2</sup> watershed. One of the assumptions in this research is that travel times of the sediment are equal. By sampling at a single point in time, the sample may only represent sources that reached the gauge by that point in the storm. Thus, the furthest point from the gauge may not be included in the suspended sediment sample. Moreover, it is assumed that all sediment travels at an equal rate—that is organic particles travel at the same rate as micaceous particles or fine sand grains or clays. K concentration data from the sediment samples indicates that this may be false. However, this was not fully explored as part of the study.

Since it is never known exactly how long a storm will last or the variation in intensity throughout a storm, not all storms were sampled at exactly the same point in the hydrograph (Appendix E). In addition, it was deemed dangerous to pull the truck close to the bank of the stream in icy conditions or darkness, so most sampling occurred during daylight.

### Tracer Selection

The Northeast Branch of the Anacostia has different physiology, geology, and land use from other watersheds where sediment fingerprinting research has been done. Therefore I did not presume to know which source groups could be differentiated by use of tracers or which tracers would be most effective for source group identification. For this reason, I measured the concentrations of 63 elements and 2 radionuclides in an initial set of sources and suspended sediment samples. Knowing the components of suspended sediment samples informed the selection of characteristics for a composite tracer fingerprint of source areas. Thus, I engaged in an iterative process whereby significant characteristics in the suspended sediments were determined at the same time as the sediment sources. Other sediment



fingerprinting researchers tend to be more economical in their choice of tracers, but that was not an option because I did not know what I would find in this watershed.

### Hypotheses

Specifically, the hypotheses tested were as follows.

- 1 Chemical analyses of sediment can be used to determine the contributions of sediment sources in urban watersheds.
- 2 Sediment source compositions used in the sediment fingerprinting of urban watersheds will include anthropogenically- enriched elements.
- 3 The primary source of suspended sediment in the Northeast Branch is derived from stream bank erosion.

In Chapter 2: Historical Patterns of Erosion and Sediment Storage, the objective was to conduct a soil survey informed by the distribution of Cs-137 and elemental Pb to show the patterns of erosion and sediment storage in this watershed. Variable land use change throughout the watershed was established using the distribution of Cs-137 and Pb. This preliminary site exploration was the basis for establishing options for grouping sediment sources.

When testing the sediment sources and suspended sediment for the 63 elements and 2 radionuclides, I found the first hypothesis to be supported but not the second. That is, chemical analyses were effective in determining sediment source groups, but those elements that were effective were not anthropogenic. So in Chapter 3, Geogenic and Anthropogenic Sources of Fine Sediment in an Urban Watershed, I show how to adjust the methodology to accommodate this anthropogenic chemical overprint from the variable land use change. Chapter 4, Quantifying Fine Sediment Sources, actually discriminates the sources and uses a mixing model to show the relative quantity of total sediment collected during the storm even was generated from each source. The banks indeed provided the most sediment, thereby supporting the third hypothesis.

## Chapter 2: Historical Patterns of Erosion and Sediment Storage Shown by Pb and Cs-137

### Introduction

In urban areas, land use and land use history can be highly variable. Land use can change from forested to agriculture to urban. Erosion can occur when forests are clear-cut or burned, when tillage disturbs soil structure and fields are seasonally bare, and when construction moves or removes the soil. Within the same land use, management practices may vary and affect rates of erosion. Agricultural methods of tilling have changed from traditional moldboard plowing to conservation tillage or no-till (Brady and Weil, 2002). More erosion occurs under deep tillage as with the moldboard plow than under conservation or no-till agricultural practices.

Urbanization resulted in an immediate erosive event as foundations were dug and land leveled for buildings. Once urbanized, much of the land is impervious and that which is permeable is largely unperturbed. These variations in land use and management each resulted in changes in erosion patterns (Wolman and Schick, 1967). As land use shifted and erosion regimes changed, pulses of sediment moved through the streams (Brady and Weil, 2002; Wolman and Schick, 1967).

For more than 30 years, Cs-137 has been used to determine rates of erosion and sedimentation (Ritchie, 2006). In the past 20 years, Cs-137 also has been used to identify the land use from which sediment originated (Ritchie, 2006). Cs-137 was atmospherically deposited during 1954-1975 with a significant increase during the year of 1964, all as a result of nuclear weapon tests. Cs-137 sorbs immediately to negatively charged soil particles and is not readily exchanged because it is monovalent, has a small hydrated radius, and a high ionic potential (Ritchie and McHenry, 1990). Cs-137 was deposited evenly over the land as atmospheric particulates, and then diluted as soil was mixed from land use change or by soil management practices.

Surface concentrations of Cs-137 therefore reflect mixing or dilution of soils. Categorizing Cs-137 into levels of zero or not detectable, medium, or high allows one to understand how the land use changes and erosion regimes affect the Cs-137 concentrations. The highest concentrations of Cs-137 are found in undisturbed areas such as forests, or where soils were translocated from undisturbed areas and not diluted (Nagle and Ritchie, 2004; Wallbrink et al., 1998). Conversely, a soil may have a Cs-137 concentration of zero under three scenarios: 1) the soil could be on a vertical surface where atmospherically deposited Cs-137 would not have come in contact with the soil surface, 2) the soil may be deep enough that it was not exposed during the years 1954-1975, or 3) a subsoil may have been exposed or relocated to a surface since 1975. Moderate Cs-137 concentrations are a result of some other perturbation—either mixing or dilution. Moderate values of Cs-137 concentration are generally associated with agricultural land. This land is plowed so the soil is perturbed by the plow. While some farmers have plowed very close to streams, the actual banks are

not plowed. Therefore, streambank soils may have moderate Cs-137 concentrations because of mixing by stream-generated erosion and floodplain deposition and/or by hillslope processes of erosion and footslope and valley deposition.

While Cs-137 is commonly used to identify land use, it is less useful in identifying sediment sources in urban areas where land use has changed rapidly over time and is variable over small areas. Pb may provide complementary information useful for determining patterns of erosion and storage in urban areas (Juracek and Ziegler, 2006).

Pb in the environment comes from atmospheric sources as does Cs-137, but also from direct deposition (Callender, 2004). Natural sources of Pb are from weathering of the Earth's upper continental crust and volcanic eruptions. Anthropogenic inputs are much greater than natural inputs in urban areas—17 mg kg<sup>-1</sup> in the Earth's upper continental crust versus 26 mg kg<sup>-1</sup> in the average soil (Callender 2004). Anthropogenic inputs of Pb into the environment generally come from fossil fuel combustion—primarily coal, municipal waste incineration, cement manufacturing, sewage sludge discharge, fertilizer application, and animal wastes.

Heightened anthropogenic inputs of Pb occurred over a specific time period. Pb was commonly used in paint and gasoline until 1978 (EPA, 2006). Pb particularly increased in the environment due to the burning of Pb alkyls in gasoline after 1940. U.S. regulation of Pb came as a result of an increase in lead poisoning, which has negative health effects on the human brain. The regulations led to a decrease from the 1970s to the 1980s of Pb emissions to the air. In the 1970s, global primary Pb emission was 449,000 metric tons but only 332,000 metric tons in the 1980s (Callender, 2004). Once these sources of Pb were limited by federal regulations in 1978, the amount of new additions of Pb to the environment sharply decreased. This peak of Pb in the environment may be used to track erosion and sediment deposition.

The study area is a watershed where the land use was converted from forest to agriculture to urban. Sediment control measures were instituted in the first half of the 1900s during the agricultural period, so the agricultural land became less erosive. The main period of urban development occurred in the 1950s (Moglen and Beighley, 2002). There are minor renovations and some in-filling, but there currently are no extensive Earth-moving operations in this watershed. Land that remains in agriculture is 26% and is located on the U.S.D.A. Agricultural Research Station. Forested land comprises 12% and is located in a protected national park (not including riparian areas with trees); the remainder is urban. This known land-use history provides an ideal location to test the combined use of Cs-137 with elemental Pb to yield historical patterns of soil erosion and sedimentation.

Therefore, I hypothesize that: 1) the pulses of sediment generated from land use changes were eroded and stored in different stream reaches; and 2) these historical erosion and sediment storage patterns can be determined by the concentrations of Cs-137 and Pb in the streambanks. Thus, by comparing the distribution of Pb with Cs-

137, the historical patterns of erosion and alluviation may be revealed in an urban watershed.

### Study Site and Methods

#### Study Site

The Northeast Branch drains to the Anacostia River, which drains to the Chesapeake Bay. The drainage area is 188.5 km<sup>2</sup>. The Northeast Branch spans two physiographic regions—the Piedmont to the west and the Coastal Plain to the east (Fig 2-1). The physiology is differentiated by the geology. The Piedmont geology primarily comprises sand-gravel facies of the Potomac Group (Patuxent Formation), which is Early Cretaceous in age. The Potomac Group is fluvially deposited quartz, with some sandstone and chert. Upland deposits of the Piedmont are fluvial sediments of the ancestral Potomac River and are of the late Miocene and Pliocene periods. The upland deposits are high in vermiculite clay. Other mapped units in the Piedmont, including the Laurel formation, are characterized by crystalline metamorphic rocks with occasional intrusions of igneous rocks. The granite, gneiss, schist, and other crystalline rocks range in age from Precambrian to late Paleozoic (Glaser, 1996; Csato et al., 2005). The Coastal Plain geology is characterized as silt-clay facies of the Potomac Group, comprised of Arundel Clay and much of the lower Patapsco Formation. The Coastal Plain in this area is highly-weathered Piedmont material from fluvial deposition. Terrace deposits are the product of stream erosion during the early Quaternary Period. The Coastal Plain ranges in age from the Cretaceous to Quaternary periods. The Piedmont physiographic region encompasses all but the southernmost reaches of the Paint Branch and the northern third of the Little Paint Branch. The Coastal Plain physiographic region includes the southern portion of the Paint Branch, the southern two-thirds of the Little Paint Branch, Indian Creek, Beaverdam Creek, and the Northeast Branch.

There is a subwatershed boundary that falls to the east of the physiographic region boundary. Four streams drain to the Northeast Branch with the Paint Branch located furthest west. The Little Paint Branch drains into the Paint Branch two-thirds the length of the Paint Branch. Indian Creek lies to the west of Beaverdam Creek, which is the easternmost stream and drains into Indian Creek three-quarters of the length of Indian Creek. The origin of the Northeast Branch is at the confluence of Paint Branch and Indian Creek.

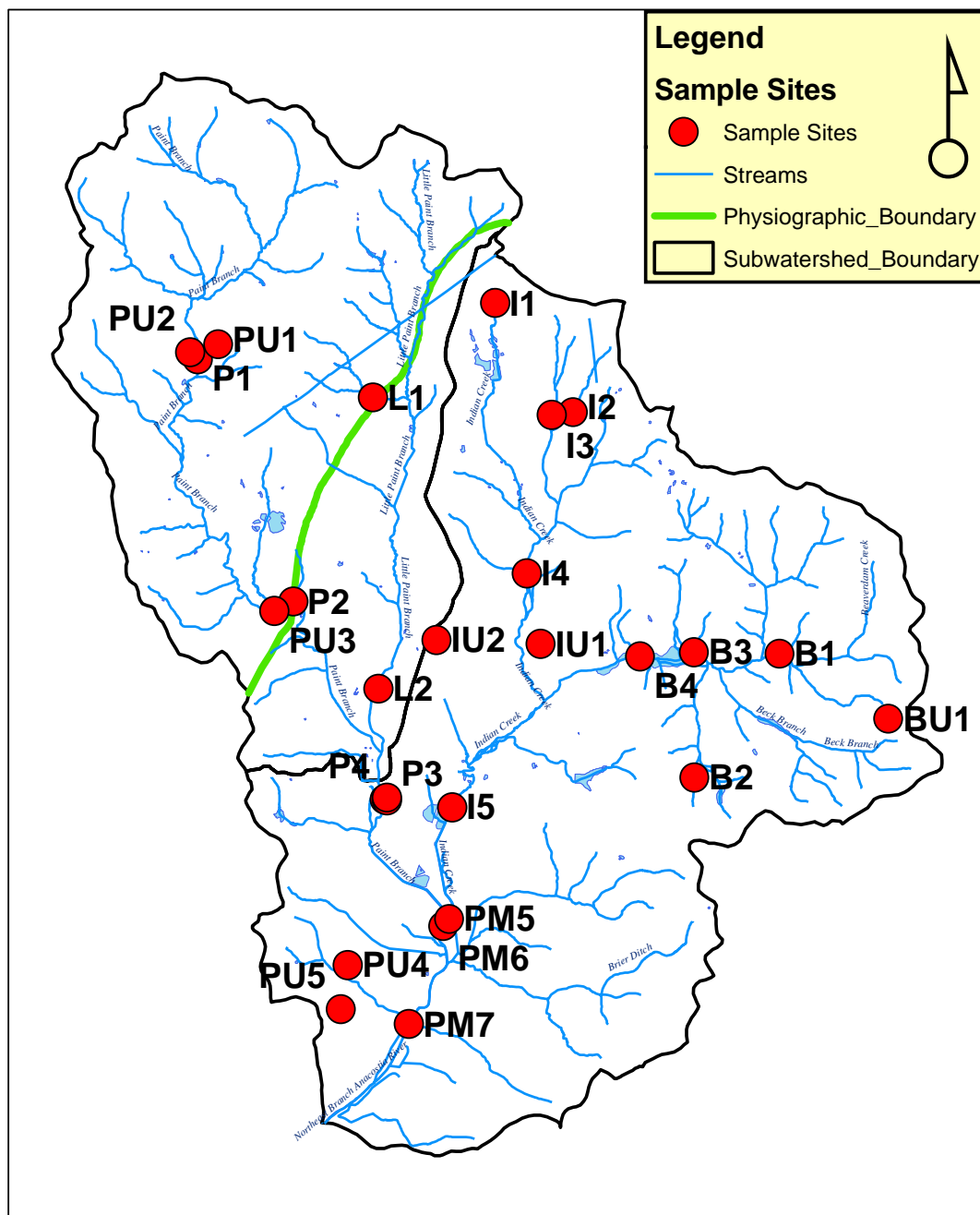


Fig. 2-1: Northeast Branch Sample Sites

Not observable on a map scale are the stream valley features and character. This topography reflects the weathering of the different geology in each physiographic region. The Piedmont is characterized by deeply incised valleys with floodplains only six m wide in many areas. While the soils are more clayey, the streams in the Piedmont are boulder and gravel bedded because the clay has washed out of the streams. The terrain is steep and hilly. In contrast, the Coastal Plain terrain is low

rolling hills with wide floodplains and streams are gravel, sand, silt or clay bottomed. The soils in the Coastal Plain are generally sandier than those in the Piedmont.

Soil series mapped in the watershed reflect the geologic parent material from which the soil formed. This parent material provides spatial discrimination across the watershed. The taxonomic designation indicates the dominant particle size in that soil. The soils in the Piedmont have more clay while those in the Coastal Plain have more sand. The stream beds in the Piedmont have gravel and bedrock remaining and the Coastal Plain has finer particle sizes remaining. In general the reservoirs of fine grain sizes are in the stream beds in the Coastal Plain or upland areas in the Piedmont; reservoirs of sand-sized particles are in the upland areas of the Coastal Plain.

The mineralogy is also designated in the taxonomic name. The soil series include those in Table 2-1, as well as the map units Mixed Alluvial Land in the Piedmont, Gravel and Borrow Pits in the Coastal Plain and Urban, Sandy and Clayey Land, and Silty and Clayey Land in the downstream mixed portion of the watershed (Soil Survey Staff, 1967). The new series names reflect the mesic temperature regime in the Mid-Atlantic region as opposed to the thermic temperature regime further south. The updated soil survey will re-map these units with the new series names and also as soils formed only in sedimentary or crystalline parent material as appropriate. Potobac, Issue or Widewater (formerly Iuka), Zekiah (formerly Bibb), and Longmarsh (formerly Johnstown) are formed in non-crystalline sediment.

Land use designations of urban, rural or forested are drawn from the National Land Cover Dataset of 2001. The land use in the area that drains to the Paint Branch and Little Paint Branch is urban, a combination of commercial and residential. The land use in the area that drains to the Northeast Branch is urban. It was primarily developed in the 1960-70s, during the height of the Cs-137 and Pb deposition time frame. Overall urban areas in the watershed are 62%. There are numerous wooded parks along the stream. The Indian Creek area is similar with the addition of gravel pits located near the stream's headwaters. Exhausted gravel pits currently are used for yard waste dumps. Atmospherically deposited Cs-137 and Pb would be diluted by these dumps.

The land use in the area that drains to Beavertown Creek is classified as rural; it is farmland owned by the USDA-ARS. Some residential areas are on the perimeter of this area. A small national forest is also included in this area. The forested portion would be expected to have the highest Cs-137 concentrations.

Atmospheric particulate matter distribution on the land may have been affected by Hurricane Agnes, a Category 1 hurricane, which reshaped much of the fluvial system in 1972. After the storm, the streams became wider as the sediment carved out the stream banks (Prepas and Charette, 2004). This single event resulted in a change in stream character still evident today. In addition, storm water and sewer pipes run alongside the streams. When the pipes were installed and subsequently patched, the

Table 2-1: Soil series in the Northeast Branch watershed

Soil Series	Physiographic Region	Taxonomic Designation	Revised Soil Series	Taxonomic Designation
Codorus	Piedmont and Coastal Plain	Fine-loamy, mixed, active, mesic Fluvaquentic Dystrudepts		
Hatboro	Piedmont and Coastal Plain	Fine-loamy, mixed, active, nonacid, mesic Fluvaquentic Endoaquepts		
Comus	Piedmont	Coarse-loamy, mixed, active, mesic Fluventic Dystrudepts		
Bibb	Piedmont and Coastal Plain	Coarse-loamy, siliceous, active, acid, thermic Typic Fluvaquents	Zekiah	Coarse-loamy, siliceous, active, acid, mesic Typic Fluvaquents
Iuka	Piedmont and Coastal Plain	Coarse-loamy, siliceous, active, acid, thermic Aquic Udifluvents	Issue or Widewater	Coarse-loamy, mixed, active, mesic Fluvaquentic Dystrudepts or Fine-loamy, mixed, active, acid, mesic Fluvaquentic Endoaquepts
Sassafras	Piedmont and Coastal Plain	Fine-loamy, siliceous, semiactive, mesic Typic Hapludults		
Sunnyside	Piedmont	Fine-loamy, siliceous, semiactive, mesic Typic Hapludults		
Keyport	Piedmont	Fine, mixed, semiactive, mesic Aquic Hapludults		
Chillum	Coastal Plain	Fine-silty, mixed, semiactive, mesic Typic Hapludults		
Johnstown	Coastal Plain	Fine-silty, mixed, superactive, mesic Pachic Argiustolls	Longmarsh	Coarse-loamy, siliceous, active, acid, mesic Fluvaquentic Humaquepts
Matapeake	Coastal Plain	Fine-silty, mixed, semiactive, mesic Typic Hapludults		
Ochlockonee	Coastal Plain	Coarse-loamy, siliceous, active, acid, thermic Typic Udifluvents		

ground was backfilled, presumably with local soil. Combined sewer overflows occur during heavy rainfall which may provide soil additions and change soil concentrations of tracers.

#### Sampling Methodology

Sites were selected to represent land use and physiography. Sample sites (16) were located at points along streams where the stream width or depth or topography changed (Fig. 2-1). To inform the selection of the sampling sites, digitized physiographic region boundary, geology, stream maps, and soils layers were overlaid using ArcGIS software. A detailed topographical map created from a 2-m DEM aided in establishing a soil-landscape model of the hydrologically active zones.

Samples of stream banks were collected by first cleaning off any plastered material from the bank's surface with a stainless steel implement. Soil was collected from the banks by scraping no deeper than five cm and vertically aggregating the sample. With few exceptions, the banks were of similar texture and color vertically. Banks were defined as those areas immediately adjacent to the stream that contain average stream flow.

#### Lab Analyses

##### **Sample preparation**

Samples were dried on paper plates in an isolated area to avoid contamination from the grinding of other samples. Sticks, leaves, roots, and garbage collected with the sample were manually removed. Samples were ground and dry-sieved to  $<63\ \mu\text{m}$ . This size fraction is the geological break between sand and silt and includes some very fine sands ( $63\text{--}50\ \mu\text{m}$ ) in the USDA particle-size classification system. Samples were sieved to allow for comparison with a comparable size fraction for a companion study.

Organic matter was not removed prior to particle-size analysis or radionuclide analysis as organic matter differences can be difficult to generalize (Walling 2005; Carter et al., 2003; Collins et al., 1997a). The sample preparation process for the elemental analysis by ICP included dissolution by  $\text{HNO}_3$ . This dissolution oxidized the organic matter and left the metals as residuals. This yielded the total elemental load for this size class, but did not discriminate between the metals sorbed to organic versus inorganic sediment.

##### **Particle-size analysis**

Particles of  $<63\ \mu\text{m}$  were analyzed with a Horiba L250 laser particle size analyzer at ARS-USDA. This method was used because it allows any particle-size range to be defined, allowing maximum flexibility. The analysis was performed in duplicate and the mean is reported in Appendix F. A laser particle-size analyzer measures the ratio of velocity in a vacuum to the velocity of light in the various particles. A refractive index of the velocity of light in clay is used.

The Cs-137 distribution in the watershed may only be understood when also accounting for the particle-size variation in the watershed. It is assumed Cs-137 sorbs immediately to the negatively charged soil and is not exchanged because it is monovalent, has a small hydrated radius, and a high ionic potential. Cs-137 adsorbs to and within the smaller clay particles which have greater surface area due to their sheet arrangement and interlayers (Ritchie et al., 1974). Thus, sand does not have sorption sites for Cs-137. Sieving a sandy sample and removing the sand-sized fraction would concentrate the particles highest in Cs-137 since the Cs-137 analysis is performed on a concentration per mass basis ( $\text{Bq kg}^{-1}$  soil). Nuclear activities are measured in Becquerels, the SI unit of radio-activity. However, as soil texture classes vary throughout this watershed, elimination of the  $>63\ \mu\text{m}$  misrepresented the bulk soil.



The >63  $\mu\text{m}$  portion of 16 bank samples was weighed to correct for biases related to variable particle size in the watershed. Correction to the measured values of Cs-137 were made by first determining the percent sand (>63  $\mu\text{m}$ ) by weight. This was done by collecting a separate sample taken from the same location as the original, weighing, sieving, and then weighing the sand fraction. The percent <63  $\mu\text{m}$  multiplied by the Cs-137  $\text{Bq kg}^{-1}$  was calculated to correct for particle size differences.

Table 2-2: Concentration of Cs-137 corrected for particle size

Site	Cs-137 ( $\text{Bq kg}^{-1}$ fine soil) Measured concentrations	% >0.63 $\mu\text{m}$ by weight	Cs_137 ( $\text{Bq kg}^{-1}$ bulk soil) Calculated concentration
B2	0.00	0.72	0.001
B1	12.12	0.82	2.130
B3	2.48	0.88	0.310
B4	8.65	0.62	3.290
I2	0.00	0.60	0.001
I3	0.00	0.75	0.001
I4	3.52	0.95	0.180
I5	4.53	0.82	0.820
L1	13.88	0.66	4.770
L2	0.00	0.74	0.001
PM5	4.28	0.90	0.450
PM6	1.99	0.81	0.380
PM7	0.00	0.89	0.001
P1	0.00	0.87	0.001
P2	0.00	0.88	0.001
Pdump	9.51	0.90	0.930

The percent of silt and clay to the bulk soil is important in regard to Pb as well. Lead hydrolyzes and some portion of Pb may have been present on oxyhydroxide sand grains coatings. For the purpose of this study, I measured only the Pb in the size fraction that includes silt and clay (<63  $\mu\text{m}$ ). The data were originally collected for comparison with fine sediment that remains suspended in the water column. For this portion of the study, the ideal data collection would have measured the Pb on the bulk soil. Since those data were not collected, and statistical correction is not possible given that the amount on sand grain coatings is difficult to estimate, only concentrations in the silt and clay fraction are reported.

#### Elemental Analysis by ICP-MS

Analysis of Pb was performed by Acme Analytical Laboratories Ltd. Pb was analyzed by ICP-mass spectrometry following a leach with 3 ml 2-2-2 HCl-HNO<sub>3</sub>-H<sub>2</sub>O (aqua regia) at 95°C for 1 hour, diluted to 10 ml. A sample-prep blank was carried through all stages of preparation and analysis as the first sample. Two reagent blanks measured background concentrations. Standard reference materials prepared by Acme using internationally certified reference materials were used to monitor

accuracy. Maximum acceptable error for precision and accuracy was  $\pm 5\%$  at concentrations  $>100\times$  the detection limit. The limit of detection is  $0.01 \text{ mg kg}^{-1}$ . A duplicate sample returned the same results within the error for precision and accuracy. While some Pb is naturally occurring, the geogenic concentration was assumed to be low and evenly deposited.

#### **Radionuclide analysis**

Radionuclide analysis was performed to determine the concentration of Cs-137. This analysis was performed by gamma-ray spectrometry using a Canberra-2000 Genie-2000 Spectroscopy System for 24 hours at the U.S. Department of Agriculture's Agricultural Research Service Hydrology Lab. The system was calibrated and efficiency determined using an analytic mixed radionuclide standard, the calibrations are traced to the U.S. National Institute of Standards and Technology. The limit of detection is  $1 \text{ Bq kg}^{-1}$  for Cs-137.

#### **Clay mineralogy**

Samples were analyzed to determine the type of clay. Unlike the other analyses performed in this study, x-ray diffraction is qualitative. X-ray diffraction was performed on 19 samples at the University of Maryland's Pedology and X-Ray Diffraction Labs to determine differences in clay mineralogy throughout the watershed. Samples were centrifuged to separate the  $<2 \mu\text{m}$  fraction. Samples were then separated into two parts and centrifuge-washed with K or Mg. The clay-oriented mounts were prepared using the filter-peel technique described in USGS File 01-041. A K and Mg mount were prepared for each sample. The K-saturated sample was analyzed at  $25^\circ\text{C}$  and subsequent heating to  $300^\circ\text{C}$  and  $550^\circ\text{C}$ . The Mg samples were placed in a desiccator over ethylene glycol and analyzed at  $25^\circ\text{C}$ . The scan was 2-30  $\theta$ .

#### **Soil Survey**

A soil survey was conducted to provide a pedological context for the study area and to inform an intuitive model that helps explain the chemical data. Auger borings were made by transects covering a catena of bank, floodplain, and upland areas. Morphological descriptions included: horizonation, texture, color, and redoximorphic features. Land cover and parent material were verified in the field. Thus, the landform and soil relationships were identified (Appendix A).

#### **Results**

Differences in the distribution of Pb and Cs-137 concentrations record the time period of deposition. As the soil eroded and moved as sediment from one part of the watershed to another, the mixing with other soils from other time periods can be estimated.

##### **Pb and Cs-137**

Within error and the limit of detection, only three sites were differentiated in Cs-137 concentration, B1, B4, and L1. The concentrations of Pb and Cs-137 did not covary,

indicating different depositional time periods or different depositional mechanisms such as direct versus atmospheric (Fig2-2).

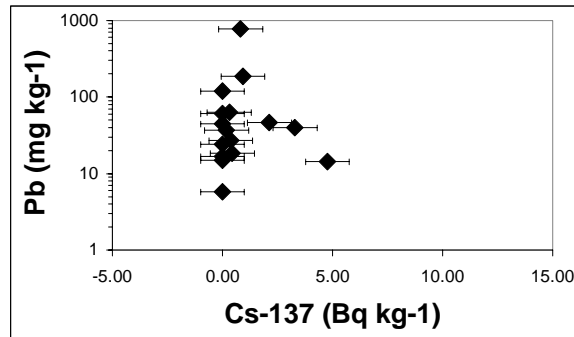


Fig. 2-2, Pb and Cs-137 concentrations.  
Error for Pb is the size of the marker.

The mean concentration of Cs-137 was  $0.82 \text{ Bq kg}^{-1}$  with a coefficient of variation (C.V.) of  $175.41 \text{ Bq kg}^{-1}$ . The mean concentration of Pb was  $43.41 \text{ mg kg}^{-1}$  and the C.V. was  $103.46 \text{ mg kg}^{-1}$ . Concentrations of Cs-137 and Pb varied by site (Table 2-3). A site-by-site description follows and is organized by stream from west to east.

Table 2-3: Tracer variation

Site	Subwatershed Boundary	Stream	Distance above gauge (m)	Cs-137 ( $\text{Bq kg}^{-1}$ bulk soil)	Pb ( $\text{mg kg}^{-1}$ fine soil)(detection limit= $0.01 \text{ mg kg}^{-1}$ )
B2	East	Beaverdam	14,855	0.00	14.40
B1	East	Beaverdam	12,173	2.13	24.10
B3	East	Beaverdam	10,168	0.31	18.50
B4	East	Beaverdam	9,468	3.29	27.20
I2	East	Indian Creek	11500	0.00	15.00
I3	East	Indian Creek	11499	0.00	5.80
I4	East	Indian Creek	10205	0.18	119.30
I5	East	Indian Creek	4744	0.82	188.20
L1	West	Little Paint Branch	17125	4.77	44.50
L2	West	Little Paint Branch	10494	0.00	46.50
PM5	Mixed	Northeast Branch	2458	0.45	63.60
PM6	Mixed	Northeast Branch	2286	0.38	39.60
PM7	Mixed	Northeast Branch	0	0.00	61.00
P1	West	Paint Branch	16385	0.00	16.70
P2	West	Paint Branch	9464	0.00	37.00
Pdump	East	Paint Branch	4744	0.93	773.20

### Paint Branch

The Paint Branch is located in the Piedmont, where stream beds are gravel and boulder bottomed and the narrow floodplains provide little opportunity for sediment

storage. The sites moving downstream are P1, P2, and Pdump. Paint Branch has little variation in Pb or Cs-137. The Cs-137 concentrations in the banks of the first order streams of the Paint Branch were less than the limit of detection of  $1 \text{ Bq kg}^{-1}$  and measured  $0 \text{ Bq kg}^{-1}$ . At sites P1 and P2, the bank is vertical and no opportunity existed for Cs-137 to have been atmospherically deposited on the vertical surface of these banks. The channels are stable and there has been little observable erosion. Site P1 is a county park and the downstream site P2 was developed pre-1950. The Pb concentration at the downstream site P2 is approximately 60% greater than at site P1. The drainage area to site P2 is also approximately 60% greater than site P1, indicating that Pb was transported and stored in the stream banks.

Site Pdump is the furthest downstream sample taken from the Paint Branch. The Cs-137 concentration was  $0.93 \text{ Bq kg}^{-1}$  compared with  $0 \text{ Bq kg}^{-1}$  at the upstream sites. At this site the Pb concentration was  $773.20 \text{ mg kg}^{-1}$ —an order of magnitude higher than elsewhere. This site was significantly incised. It had ~2 meters of fill material over Cretaceous-aged sediments. The fill material was partially the result of the site being used as a garbage dump located directly alongside the stream. Historical photos and materials found at the site, such as a pipe with a manufacture date of 1859, confirm this. The opposite side of the bank, where there was no evidence of a garbage dump, measured  $14.9 \text{ mg kg}^{-1}$  of Pb and  $0 \text{ Bq kg}^{-1}$  of Cs-137—levels commensurate with other samples taken from that stream (see Chapter 4 for data from additional samples).

#### **Little Paint Branch**

The Little Paint Branch headwaters are in the Piedmont and downstream is in the Coastal Plain, all of which is in the west subwatershed. The sites on the Little Paint Branch are L1 and L2, which had variable concentrations of Cs-137 in the banks. Upstream site L1 had  $4.77 \text{ Bq kg}^{-1}$  Cs-137 compared to  $0 \text{ Bq kg}^{-1}$  at downstream site L2. At the upstream sample site L1, the stream is incising and widening. Site L1 is located in a residential area that was developed around 1995. This site is immediately downstream from a bridge where the stream is piped underneath a road. The presence of a Bw horizon indicates a fairly young soil. It is possible that the entire surface and subsurface drainage network was changed as the residential area and an adjacent golf course were developed. Prior to development, the area was farmed. The stream may naturally migrate and may now be running through soils eroded from the hillslope. Construction practices moving subsoil to the surface combined with erosion via soil creep downslope may have diluted soil from the Cs-137 depositional period.

The fine sediment to which the Cs-137 is sorbed appears to have been transported further downstream as indicated by the decrease in Cs-137 stored in the banks at site L2. At the downstream site L2, there is a floodplain over a pre-1950 soil. There is a lithologic discontinuity in some reaches of the stream bank that indicates that the floodplain overlies an older soil which overlies an even older soil. The cobble line in the bank sediments reveals an active floodplain where the stream migrates.

The Pb concentrations of  $44.5 \text{ Bq kg}^{-1}$  at site L1 and  $46.5 \text{ Bq kg}^{-1}$  at site L were the same within the margin of error indicating soil stability prior to 1954 when Pb was being used in gasoline but Cs-137 was not yet deposited.

The Little Paint Branch appears to have soil older than that which has Pb and Cs-137 deposited on it. The newer sediment deposits are of a sandier texture, which has little Cs-137 sorption capacity.

### **Indian Creek**

Indian Creek is located in the Coastal Plain where the soils are sandier and the streambeds are finer textured. Valleys are wide and the topography is not as steep as the Piedmont. Sites on Indian Creek include I2, I3, I4, and I5, which is downstream from the Beaverdam confluence. On Indian Creek, Cs-137 and Pb concentrations systematically increased in a downstream progression. Cs-137 was found at  $0 \text{ Bq kg}^{-1}$  at both headwater sites I3 and I2, both sites have vertical banks. These sites are close to the headwaters so there is not a lot of sediment being transported. Site I3 was Cretaceous-age stratigraphy. At site I2, the soil is older than the 1950s. While the trees in the riparian buffer are fairly young ( $<60$  years), the soil did not have an Ap horizon, so it was not farmed. The stream is in a bottom-land and is flooded too often to be farmed. While the banks are not high, they are vertical. Cs-137 would not have been deposited on these banks.

Pb concentrations measured  $5.8 \text{ mg kg}^{-1}$  at site I3 and  $15.0 \text{ mg kg}^{-1}$  at site I2. The concentrations vary according to the distance to paved road and parking lots. While Pb was atmospherically deposited, it is possible that some gasoline leaked directly into the soil near the sample site from farm machinery.

At site I4, the channel banks are vertical. The stream is widening and may be intercepting a soil on which radionuclides were deposited during the 1954-1974 time period. The moderate Cs-137 concentration of  $0.18 \text{ Bq kg}^{-1}$  at site I4 reflects the channel widening. The Pb dramatically increased from its upstream measured concentration to  $119.3 \text{ mg kg}^{-1}$ . Since this site is in an industrial zone with many automobile repair businesses, it is possible that direct leaks to the soils and stream occurred.

At site I5, both Cs-137 and Pb increase to  $0.82 \text{ Bq kg}^{-1}$  and  $188.2 \text{ mg kg}^{-1}$  respectively over concentrations measured upstream. This site is located near where there historically has been industry, though now some of the industrial sites have been replaced by residential areas. Active erosion and sedimentation is illustrated by a half-exposed tire in a horizontal position in the bank of site I5; the tire could only be moved and deposited by the stream. Indian Creek widened during the current hydrological regime. The hydrologic regime change is caused by greater storm water fluxes, which are a result of increasing impervious surfaces. Levels of Cs-137 and Pb generally increase moving downstream showing sediment storage in the Indian Creek.

### **Beaverdam Creek**

Beaverdam is located in the Coastal Plain and the sites on this stream are B1, B2, B3, and B4. Beaverdam Creek varies in terms of sediment storage and erosion sites. The pattern of different erosive reaches of the stream and storage stream reaches is most obvious on Beaverdam Creek. At sites B2 and B3 erosion was evident and at sites B1 and B4 deposition was evident. The Cs-137 and Pb concentrations were higher at the depositional sites than at the erosional sites.

Site B1 is the furthest upstream sample on the main branch of this creek. The soil profile for site B1 indicates that this site had undergone some soil structure formation, which would not be evident if the soils were solely unconsolidated sediments. Therefore, the stream cut or broadened the channel into an older soil. The area around this stream is a floodplain, as shown by both the soil and elevation. The area is wooded and could not have been farmed recently, although there is a farm upslope. Thus, the Cs-137 concentration of  $2.13 \text{ Bq kg}^{-1}$  supports the hypothesis that the stream cut a new channel or broadened the channel since Cs-137 was deposited. The pedological evidence of soil structure formation is that there has been deposition, or sediment stored, in the stream banks and does not indicate that sediment was deposited from an upstream site. Pb was measured at  $24.10 \text{ mg kg}^{-1}$ .

Site B3 has a typical floodplain profile with buried A horizons interspersed with newly forming soils and older, more developed soils. As the stream has either held its channel, allowing soil development, or meandered and deposited sediment over older soils while cutting into those older soils, sediment has been translocated. The area is forested with trees > 80 years old. Upslope is farmed, but not the floodplain. Bars were observed moving downstream and active erosion is occurring. This meandering and sediment storage has resulted in mixing, which is evident in the  $0.31 \text{ Bq kg}^{-1}$  of Cs-137 found in the banks. The Pb concentration of  $18.5 \text{ mg kg}^{-1}$  is less than that found upstream indicating active erosion of the fine sediment that had been in storage.

Downstream, Beaverdam Creek opens up into a marsh where there is evidence of rapid changes in the path of the stream. In the seven months following sampling, the bank sample site became a small island in the middle of the stream. At site B4, the Cs-137 concentration increases to  $3.29 \text{ Bq kg}^{-1}$  which is greater than any upstream measurement. Either the bank is new and was from an undisturbed area, or the sediments forming the bank were translocated from an area of undisturbed land. The site is an area of sediment storage, and either explanation is equally defensible. Pb concentrations followed the same trend and were measured at  $27.2 \text{ mg kg}^{-1}$ .

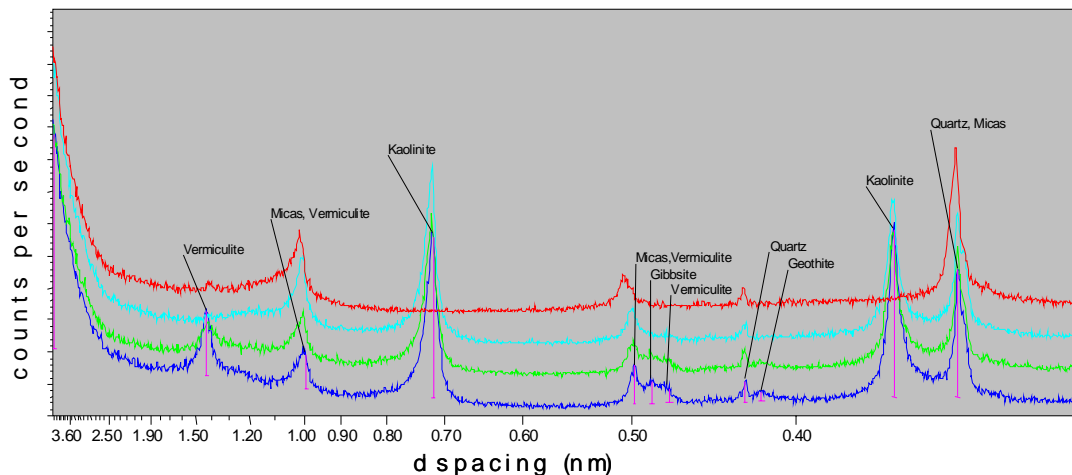
Site B2 is at the headwater of a small tributary leading into Beaverdam Creek. It is sandwiched between a small road and large parking lot in an apartment complex and a highly trafficked freeway (Baltimore-Washington Pkwy). This tributary's headwaters are drainage pipes for storm runoff. The soil around the stream is highly variable and disturbed. The  $0 \text{ Bq kg}^{-1}$  Cs-137 concentration reflects a subsoil fill was used. Pb was measured at  $14.4 \text{ mg kg}^{-1}$ .

### Northeast Branch

Sample sites on the Northeast Branch progress downstream from site PM5 where Indian Creek and Paint Branch come together, to site PM6 which is a backwater channel, to site PM7 where the banks are hardened with large, cut granite rocks. The hardening of the banks is effective and prevents stream bank erosion or channel widening. However, at sites PM5 and PM6, the stream has been able to incise as well as widen. Cs-137 was  $0.45 \text{ Bq kg}^{-1}$  and Pb was  $63.6 \text{ mg kg}^{-1}$  at site PM5. At site PM6, the backwater channel, Cs-137 decreased slightly to  $0.38 \text{ Bq kg}^{-1}$  and Pb decreased to  $39.6 \text{ mg kg}^{-1}$ . At site PM7, there was  $0 \text{ Bq kg}^{-1}$  Cs-137 and Pb was measured at  $61.0 \text{ mg kg}^{-1}$ . The banks that are now exposed were formed from channel widening into what had been a floodplain—where Cs-137 would have accumulated during the period of nuclear testing. Cs-137 values at sites PM5 and PM7 indicate mixing from an incising channel (where there was a zero concentration of Cs-137 as older soil is exposed on vertical bank faces) and a higher measurement of Cs-137 (from the widening channel into older soils). Incision without additional widening at site PM7 is supported by the zero concentration of Cs-137 at site PM7.

### Clay Mineralogy

The results of the clay mineralogy analysis did not show significant, identifiable differences throughout the watershed. For example Site P2, located in the Piedmont does not contrast significantly with Site B1, located in the Coastal Plain (Fig. 2-3). The scans show vermiculite, mica, kaolinite, quartz and some gibbsite and goethite present in both physiographic regions. The vermiculite peak had shoulders in several of the scans, indicating hydroxy-interlayered vermiculite. The size of the peak is not indicative of the dominance of that mineral and can not be used to calculate relative differences. This analysis was discontinued after 19 samples as the results did not distinguish among soil samples.



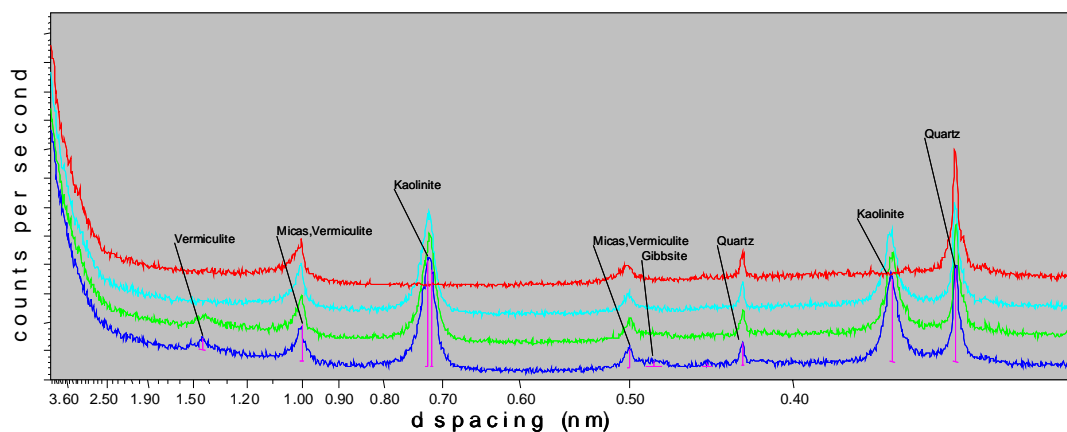


Fig.: 2-3 Clay mineralogy, P2 bank (top) and B1 bank (bottom)

### Soil Survey

A site-by-site soil description illustrates the differences among the soils and streams in this watershed (Appendix A). As land development occurred, the effect on the streams differed according to the topography and particle size in the streambanks and bed. Those streams that were boulder and gravel bottomed have limited fine sediment, and the banks were not built during small floods. These streams became more deeply incised with time except where the stream bottoms were bedrock; these bedrock-bottomed streams widened. In the Coastal Plain, there were wider floodplains and these developed where the land was not impervious from urban development. However, urbanization increased the size of floods because storm water was efficiently eliminated from the impervious surfaces and piped into the streams at high velocities. With fewer small floods due to the storm water management system, channel widths and depths have enlarged to accommodate the more frequent higher discharges (Konrad et al., 2005). Thus, streams are not going overbank and depositing sediment loads so floodplains in the Coastal Plain are not being built as they were in the past. The soil descriptions show that each site varies based on land use history and stream character.

### Discussion

While there were distinct land use differences in the watershed, the patterns of Cs-137 and Pb concentrations in the streambanks did not differentiate these differences. This is because there is a distinct reach of the streams that provides sediment storage in this watershed. This reach falls between the headwater portion, which is erosional, and the downstream portion, which has no place for storage because banks are hardened and floodplain access restricted. The distributions of Cs-137 in the Northeast Branch watershed shows an increasing concentrations of Cs-137 in the progression downstream until the region where the channels are hardened and sediment storage is no longer possible. The exceptions to this increase are the two wetland areas along Beaverdam Creek (B1 and B4). Wetland stream channels



frequently carry less discharge. This causes the stream flow to go overbank and create and/or maintain the riparian wetland. Sediment is carried and deposited in the riparian wetland.

Sediment storage occurred in the middle swath running east to west in the watershed. The banks in these reaches were built from either transported bank materials from eroding banks moved downstream or overland flow moving upland materials to the floodplains. The banks are carved from these floodplains.

In the downstream area of the watershed, Cs-137 concentrations were never above the watershed mean for the Northeast Branch downstream portion of the watershed. The streams were channelized and hardened in these downstream areas; there was no storage and Cs-137 concentrations reflected this by decreasing back to zero, as they were in deeply incised and vertical bank stream reaches.

Pb can be a point-source pollutant whereas Cs-137 is only atmospherically deposited; the two confound each other. Pb concentrations seem to be a better indicator of level of traffic and distance to stream than time period of development (Juracek and Ziegler, 2006). This indicates that Pb in this watershed was primarily directly deposited. If Pb were atmospherically deposited, it would track time period of development. To fully understand historical trends in Pb and Cs-137 deposition, samples should be taken at depth increments in the banks along each reach of the stream.

Correcting for particle-size differences in the watershed was necessary because the amount of Cs-137 and Pb or any other tracer is commonly measured in units of mass. By biasing the mass through removal of large particle sizes, some soils will have values that are diluted or concentrated in comparison to the land from which they came. This is only an issue where an understanding of the land is important. If the measurements are used only for comparison to other fine sediment sources such as the suspended load, then the patterns across the landscape are not relevant. Statistically correcting particle size to reflect bulk soil for Cs-137 concentrations assumes that Cs-137 does not adsorb to sand particles. I made this assumption because Cs-137 is monovalent and has a small hydrated radius. In contrast, Pb is known to sorb to sand particles as Pb hydrolyzes in the oxyhydroxide coatings. I was unable to make a statistical correction for Pb because of the lab procedure.

Erosion was episodic and therefore difficult to track with depth integrated samples. Episodes were caused by land use and management changes as well as by single exceptional storm events like the hurricane (Nicholas et al. 1995).

Atmospherically deposited Cs-137 shows that erosion and sedimentation varies by stream reach in this watershed. The directly deposited Pb was less useful to understanding the historical erosion and sedimentation in this urban watershed.

## Chapter 3: Geogenic and Anthropogenic Sources of Fine Sediment in an Urban Watershed

### Introduction

Suspended sediment is a water quality problem because it blocks sunlight from permeating water, suppresses subaquatic vegetation growth, smothers the benthic biota that live among the plants, and carries contaminants (EPA, 2006c). When transported, sediment moves contaminants into and through waterways. Particles  $<63\ \mu\text{m}$  are the most important sediment fraction since it is these fine particles that stay in suspension and carry the bulk of the contaminants (Vanoni, 1975; Marvin et al., 2004; Tuccillo, 2006). Sources of fine suspended sediment may be present where there is little visible evidence of erosion. Also, the amount of fine sediment from sandy soils may be small, even if erosion is high. Sand-sized particles quickly settle and therefore do not carry toxins long distances or impact light attenuation in downstream water bodies. Fine sediment sources have been successfully quantified using a sediment fingerprinting approach (Collins et al., 1997a; Walling et al., 1999; Motha et al., 2003; Walling, 2005).

The sediment fingerprinting approach compares suspended sediment to sources, and determines the relative quantity from each source. One of the difficulties in quantifying sources of sediment is determining parameters for classifying the sources into groups. Previous researchers have parameterized sediment sources by land use (e.g., forested, agricultural, or industrial), geological formations, soil map units, or a combination of these classifications (Deboer and Crosby, 1995; Collins et al., 1997a; Walling et al., 1999; Motha et al., 2003; Walling, 2005; Gellis and Landwehr, 2006).

Urban watersheds present unique challenges. Chemical or biological waste from human activities may sorb to the sediment that moves through the watershed (Boruvka et al., 2005). The spatial pattern of this anthropogenic imprint may vary among urban areas. In addition, the change in land use to urban does not necessarily happen simultaneously throughout the watershed. A non-linear rate of urbanization combined with a complicated spatial pattern of urbanization adds complexity to using land use as a sediment source parameter when a variable urban imprint is present. A method is needed to differentiate fine sediment in urban watersheds.

I hypothesized that chemical analyses of sediment could be used to determine end-member compositions of sediment in urban watersheds. Furthermore, I hypothesized that end-member compositions used in the sediment fingerprinting of urban watersheds included anthropogenically enriched elements. Also, I provide a method for differentiating fine sediment by the level of enrichment of trace elements compared to the mean composition of the Earth's upper continental crust.

Radionuclide and element concentrations are used in this study as sediment tracers. Elemental concentrations may originate from the bedrock, or from atmospheric

inputs, and other anthropogenic activity. In this urban watershed, sediment sources include water-transported material from streets and the deposition of atmospheric particulate matter, in addition to eroded soil from fields and stream banks. Atmospheric particulate matter falls on soil surfaces and pavement with little seasonal variation (Almeida et al., 2005). Automobiles also produce particulates from tires and exhaust. All of these particulates accumulate and wash into streets and down storm drains that discharge to streams. The tracers used in previous research are generally fewer in number than those for which I tested (Collins et al., 1997a; Walling et al., 1999; Motha et al., 2003; Walling, 2005; Gellis and Landwehr, 2006). I considered a broader number of trace elements because an urban watershed may have different tracers present than agricultural and forested watersheds, where sediment fingerprinting is more commonly used.

### Study Site and Methods

#### Study Site

The study area was the watershed of the Northeast Branch of the Anacostia River in Maryland located approximately 16 km northeast of Washington, D.C. (Fig. 3-1). Four main tributaries make up the Northeast Branch watershed. From west to east they are: Paint Branch, Little Paint Branch, Indian Creek, and Beaverdam Creek. The Little Paint Branch drains to the Paint Branch. Beaverdam Creek drains to Indian Creek. The confluence of Paint Branch and Indian Creek form the Northeast Branch of the Anacostia. The Anacostia River drains to the Chesapeake Bay. The drainage area of the Northeast Branch watershed is 188.5 km<sup>2</sup>.

The Northeast Branch watershed spans two physiographic regions – the Piedmont and the Coastal Plain. The different geological composition of the two physiographic regions results in distinguishable elemental concentrations that may be used as natural tracers. The physiographic province reflects the geology and topography. Coastal Plain geology primarily comprises silt-clay facies of the Potomac Group (Patuxent Formation), which is Early Cretaceous in age. The Potomac Group is fluvially deposited quartz, with some sandstone and chert. The Coastal Plain also includes Arundel Clay and much of the lower Patapsco Formation. The Coastal Plain in this area is highly weathered Piedmont material from fluvial deposition. Upland deposits of the Coastal Plain are fluvial sediments of the ancestral Potomac River and are of the late Miocene and Pliocene periods. Terrace deposits are the product of stream erosion during the early Quaternary Period. These are primarily unconsolidated sediments. The Coastal Plain ranges in age from the Cretaceous to Quaternary periods.

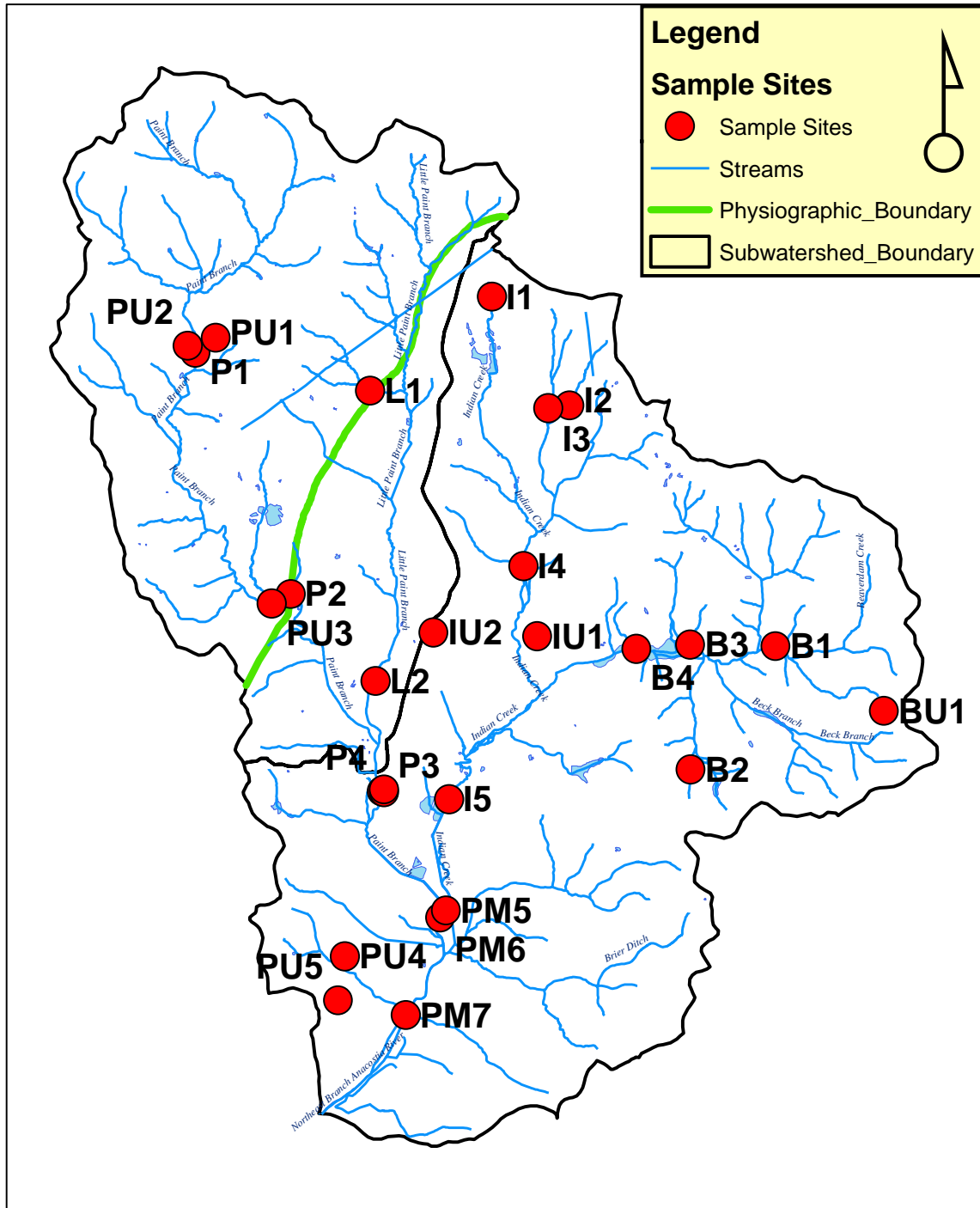


Fig. 3-1 Northeast Branch Watershed sample sites.

Mapped units in the Piedmont, including the Laurel formation, are characterized by Precambrian crystalline metamorphic rocks with occasional intrusions of igneous rocks. The granite, gneiss, schist, and other crystalline rocks range in age from Precambrian to late Paleozoic. Piedmont upland deposits are high in vermiculite clay (Glaser, 1996; Csato et al., 2006).

In addition to encompassing two physiographic regions, the Northeast Branch watershed is made up of two subwatersheds. The west subwatershed is influenced by Piedmont geology and the east subwatershed is characterized by Coastal Plain geology (Fig. 3-1). The subwatershed boundary is mapped east of the physiographic boundary and is located between Little Paint Branch and Indian Creek.

In the west subwatershed the land use is urban—a combination of commercial and residential. There are numerous wooded parks along the stream. In the east subwatershed land use is industrial, commercial, residential, forested, and agricultural. Land use around Indian Creek includes industrial, commercial, and residential areas. The land use in the area that drains to Beaverdam Creek is rural and has long been managed as farmland by USDA-ARS. Some residential areas are on the perimeter of the land that drains to Beaverdam Creek. A forested national park is also located in the east subwatershed.

Presently the Anacostia River watershed, which includes the Northeast Branch watershed, is 64.6% urban, 26.6% forested, 8.1% agricultural, 0.2% wetlands, and 0.4% other categories (Maryland Department of Natural Resources, 2000). Impervious land is 33.2% (Maryland Department of Natural Resources, 2000). The Northeast Branch area of the Anacostia was developed primarily between 1960 and 1970. While minor construction projects are currently taking place, there are no current wide-spread Earth-moving projects.

#### Sample Locations

Sample locations were located along reaches of each of the four tributaries and the main stem to represent each subwatershed, landscape position, and land use of the Northeast Branch watershed (Fig 3-1, Appendix B).

The high percentage of impervious surfaces necessitated more soil samples from banks because much of the upland area was paved. Of the bank samples, there were three sample sites along the Paint Branch, two along the Little Paint Branch, four along Indian Creek, five along Beaverdam, and three along the Northeast Branch. Bank sample sites were chosen where stream width or depth changed, topography changed, there was a confluence, or significant erosion was visible.

These geomorphic changes in the stream areas indicated a possible change in soils and sediments. At five of these stream bank sites, samples were taken along a transect moving away from the bank to include the landscape positions of stream bank, floodplain, and upland. Depending on the topography, the upland position was either a backslope or a summit position. These five sites were selected to represent physiographic region and land use.

Additional sediment inputs in this urban area include street residue, sewage, and atmospheric particulate matter. Street residue was collected for both physiographic regions in the urbanized portions of the watershed. One construction site located adjacent to the stream and very near the suspended sediment collection site was

sampled as were four point bars. It was outside the scope of this project to collect sewage or atmospheric particulate matter. However, atmospheric particulate matter data was available from other watersheds for comparison. Suspended sediment samples were collected at the outlet of the Northeast Branch watershed (Fig. 3-1, PM7). The distribution of the sediment samples is presented in Appendix B.

#### Sampling Methodology

##### ***Sediment source samples***

A total of 35 sediment source samples were collected. The stream banks were defined as those areas immediately adjacent to a stream that contain the stream at average flow. Floodplains were defined as those areas that are broad flatlands on either side of a stream that accommodate maximum flood capacity. All other areas were classified as upland.

For floodplain and upland areas, surface samples were collected 2-5 cm deep with a stainless steel implement. Bank samples were collected by first scraping away any plastered material, and then aggregating sediment vertically throughout the bank. With few exceptions, each bank profile was of similar texture and color vertically. Full descriptions of stream banks in this watershed are in Appendix A.

Street residue was collected by sweeping the street 3.0 m on either side of a storm drain located on a street adjacent to a stream. Streets were swept with a clean plastic-bristled broom from the center of the street to the curb on both sides of the street (Breault et al., 2005). Street residue samples were collected by aggregating residue from six different streets. To represent seasonal variation, samples were collected just after leaf fall in fall 2005 and in late spring 2006. The intervening winter was atypically dry with little snowfall, so salt was not broadly applied to streets. Accordingly, a winter sample was not collected.

##### ***Suspended sediment samples***

Samples were collected when rainfall covered the entire watershed and when the sediment load was most concentrated. Samples of sediment were collected for comparison to the sources to determine the sources of suspended sediment and the characteristics of each source.

The Northeast Branch watershed is located at 38° and 39° N, 76° and 77° W. The climate is humid temperate with an average temperature of 13.2 °C and an average annual rainfall of 117 cm (NOAA, 2005). There are four distinct seasons with mild winters. Rainfall is evenly distributed throughout the year; storms with broad aerial extent occur primarily in winter months. There are isolated thunderstorms in the summer that deliver rain quickly and create flashy stream flow. These summer thunderstorms typically do not span the entire watershed.

Suspended sediment collection was targeted for high sediment generating events. Suspended sediment is most concentrated during the initial runoff period of a storm

when precipitating conditions have been wet (Appendix E). Sampling was targeted for saturated overland flow conditions.

Weather forecasts were monitored via real-time forecasts (University of Maryland Department of Meteorology and NOAA). In addition, a rain gauge eight km from the site was monitored at least three times per day. When rainfall was close to 2.5 cm, the Northeast Branch was visited and assessed for sediment movement into the stream by visual assessment of the Tyndall effect in the stream water, gauge height, and amount of overland flow. Samples were not collected when unsafe conditions existed due to darkness or excessive ice on the roads.

Sampling occurred at one location and depth under a bridge where the stream was well mixed. A trash pump was placed into the stream where the current held it above the stream bed but below the surface of the water. Particles  $<63\ \mu\text{m}$  are well mixed in the water column, so it was not necessary to collect at a particular depth (Vanoni, 1975). The stream water was pumped into three 208-liter steel barrels lined with round-bottomed plastic bags.

Eight suspended sediment samples were collected for one year (July 1, 2005 to June 30, 2006) to account for seasonal differences in erosion and run off. Collection dates and flood information are in Table 3-1. The fine sediments are on average 25% of the total load carried in the stream. The larger particles do not travel far downstream, but settle out of the water column.

#### Lab Analyses

##### *Sample Preparation*

Sediment source samples were brought back to the laboratory and air dried on paper plates in an isolated lab to minimize cross contamination. Visible leaves, twigs, and garbage in the samples were removed manually. Samples were then ground using a mortar and pestle. In order to avoid concentrating or diluting source areas based on particle size, the samples were dry sieved to  $<63\ \mu\text{m}$  using a shaker, which restricted analysis to the dominant size class in the suspended sample.

Suspended sediment samples were prepared by removing the stream water from the barrels within one week following collection. A Teflon-lined continuous centrifuge was used for sediment removal. The centrifuge was selected because the Teflon lining would prevent metal contamination from the machine itself. Suspended sediment samples were dried in an oven at  $60^\circ\text{C}$ . The suspended sediment samples were also ground and dry sieved to  $<63\ \mu\text{m}$  using a shaker.

Organic matter was not removed from any of the samples prior to radionuclide analysis. Organic matter differences are complex and difficult to generalize, therefore even where significant organic matter is present, corrections are frequently not made (Walling, 2005). The sample preparation process for the elemental analysis by ICP includes dissolution by  $\text{HNO}_3$ . This dissolution oxidizes the organic matter and leaves the metals as residuals. This yields the total elemental load for this size class, but does

not discriminate among the metals sorbed to organic versus inorganic sediment (Sun et al., 2001; Impellitteri et al., 2002). In all of the source samples, total carbon was < 9.9%.

For the particle-size analysis, organic matter was removed by H<sub>2</sub>O<sub>2</sub> only from the street residue samples. Without organic matter removal a great many particles were not spherical and blocked laser detection of the smaller particles, leading to an overestimate of particle size. These non-spherical particles are thought to be leaves and grass clipping that were crushed or ground by automobile traffic.

Table 3-1: Suspended sediment sample characteristics. \*\*at last available time before gauge failed.

Date and time of suspended sediment collection	Q at time of suspended sediment collection (m <sup>3</sup> s <sup>-1</sup> )	Date and time of hydrograph peak	Q at hydrograph peak (m <sup>3</sup> s <sup>-1</sup> )	Sediment collected (g m <sup>-3</sup> )	<0.63 µm Sediment (g m <sup>-3</sup> )	%<0.63 µm sediment/bulk sediment collected	Sediment flux at time collected (g s <sup>-1</sup> , <0.63 µm)
10/7/2005 at 12:30	15.51	10/8, at 7:00	55.87	23.05	8.21	36%	127.37
10/22/2005 at 9:00	0.83	10/22 at 9:30	2.16	250.72	53.76	21%	44.67
12/25/2005 at 15:00	0.33	12/25 at 18.15	3.32	105.46	31.57	30%	10.52
1/18/2006 at 9:00	4.00	1/18 at 11:45	10.55	175.12	37.56	21%	150.15
2/4/2006 at 16:00	0.80	2/4 at 21:00	6.61	120.7	31.99	27%	25.58
4/23/2006 at 6:05	1.46	4/22 at 21:00	9.09	623.46	199.33	32%	290.63
5/11/2006 at 20:30	0.39	5/11 at 21:00	4.24	114.2	15.914	14%	6.24
6/25/2006 at 11:45	14.39	6/25 at 20:30 **	173.72**	293.09	62.23	21%	31613.37

#### ***Radionuclide analysis***

Radionuclide analysis was performed on sediment source samples and suspended sediment samples by gamma-ray spectrometry using a Canberra-2000 Genie-2000 Spectroscopy System for 24 hours at the U.S. Department of Agriculture's Agricultural Research Service Hydrology Lab. By running the sample for the long duration, lower levels may be quantified. The limit of detection is 1.00 Bq kg<sup>-1</sup>. The system was calibrated and efficiency determined using an analytic mixed radionuclide standard; the calibrations are traced to the U.S. National Institute of Standards and Technology.



### ***Elemental analysis by ICP-MS and ICP-ES***

The elemental analysis was performed by Acme Analytical Laboratories Ltd. ICP-emission spectrometry was performed following a  $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$  fusion at  $980^\circ\text{C}$  and dissolution in 0.5%  $\text{HNO}_3$ . The lithium borate fusion lowers the boiling point allowing complete dissolution of the silica. Rare Earth and refractory elements were tested by ICP-mass spectrometry following the same fusion and dissolution process. Total carbon and sulfur were determined by LECO. Loss on ignition (LOI) was determined by weight difference after ignition at  $1000^\circ\text{C}$ . The elements and method for each are in Table 3-2.

The elemental analyses were performed on all the sediment source samples as well as the suspended sediment samples. A sample-prep blank was carried through all stages of preparation and analysis as the first sample. Two reagent blanks measured background. Standard reference materials prepared by Acme using internationally certified reference materials were used to monitor accuracy. Maximum acceptable error for precision and accuracy was  $\pm 5\%$  at concentrations  $>100\times$  the detection limit. The limits of detection are in Appendix D. A duplicate sample returned the same results within the error for precision and accuracy.

Table 3-2: Element analytical methods

<b>Method</b>	<b>Chemical Tracer</b>
$\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ fusion analysis by ICP-ES.	$\text{SiO}_2$ , $\text{Al}_2\text{O}_3$ , $\text{Fe}_2\text{O}_3$ , $\text{MgO}$ , $\text{CaO}$ , $\text{Na}_2\text{O}$ , $\text{K}_2\text{O}$ , $\text{TiO}_2$ , $\text{P}_2\text{O}_5$ , $\text{MnO}$ , $\text{Cr}_2\text{O}_3$ , Ni, and Sc
LECO	Total C, Total S
Rare Earth and Refractory Elements: $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ fusion analysis by ICP-MS	Ba, Be, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, Zr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
Leach with 3 ml 2-2-2 $\text{HCl-HNO}_3\text{-H}_2\text{O}$ (aqua regia) at $95^\circ\text{C}$ for 1 hour, diluted to 10 ml, analyzed by ICP-MS.	Mo, Cu, Pb, Zn, Ni, As, Cd, Sb, Bi, Ag, Au, Hg, Tl, Se

### ***Statistical Analyses***

Tracer concentrations of sediment source samples were examined for normality using SAS v. 9.1 (SAS Institute Inc., 2004). Analysis of probability plots and box plots indicated non-normally distributed data, and not all elements were skewed in the same direction. Normality was violated, so non-parametric tests were used. In addition, there were orders of magnitude among the tracers, so ranking the data allowed for comparison.

The source samples were grouped to minimize variation within source groups while maximizing variation among source groups. I examined a Spearman correlation matrix for various groupings of elemental and radionuclide concentrations. The non-parametric Kruskal-Wallis means comparison test was used to identify the tracers with significant differences among source groups. Tracers that failed this test ( $p < 0.05$ ) were removed.

The sediment sources were grouped by subwatershed and landscape position. These groups were further parameterized on the level of enrichment in various elements compared to the mean elemental composition of Earth's upper continental crust.

## Results

### Sediment Source Characterization

The tracers did not clearly discriminate sediment sources when grouping by land use, upstream vs. downstream sections of the streams, or even by each stream. Results of the physiographic region sediment source grouping were similar to the subwatershed grouping. However, the subwatershed grouping was more powerful than the physiographic region. Significant differences were present between the west subwatershed and east subwatershed for the tracers in Table 3-3. The west subwatershed was enriched in all of these elements except for As, Cr<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and Zn. The west subwatershed is influenced by the Piedmont physiographic region; the enrichment is predominantly from elements native to the metamorphic rocks in that region. In contrast, the east subwatershed includes the more highly weathered Coastal Plain physiography that is depleted in these elements. The soils in the east subwatershed are sandier, which is reflected in the elevated SiO<sub>2</sub> concentration.

The tracers that were significantly different when grouped by landscape position are listed in Table 3-4. The banks were enriched in Dy, Eu, Gd, La, Lu, Tb, and Tm. The floodplains were enriched only in Cs-137, while the point bars were enriched in Er, Hr, Ho, K-40, Sn, TiO<sub>2</sub>, Y, Yb, and Zr. Street residue was enriched in Cu and Mo. Upland samples were enriched only in P<sub>2</sub>O<sub>5</sub>.

More tracers were elevated in the bank and point bar landscape positions than any other position (7 and 9 respectively compared to  $\leq 2$  in any other group). The banks and point bars are the landscape positions where soil is most likely to move into stream flow. When examined on a pair-wise basis, the banks and point bars cannot be discriminated from each other. The point bars were not considered in further analysis. Moreover, point bars represent temporary storage of sediment from other sources.

Table 3-3: Tracers that differentiated by hydrological subwatershed boundary ( $p < 0.05$ ). Bold indicates higher concentration.

Tracer	Units	Kruskal-Wallis	West mean (no.=13)	East mean (no=19)
Al <sub>2</sub> O <sub>3</sub>	wt. %	0.000	<b>15.02</b>	9.70
As	mg kg <sup>-1</sup>	0.037	3.02	<b>4.52</b>
Ba	"	0.000	<b>508.88</b>	310.69
Be	"	0.003	<b>2.92</b>	1.63
Bi	"	0.000	<b>0.36</b>	0.18
CaO	wt. %	0.026	<b>0.35</b>	0.33
Ce	mg kg <sup>-1</sup>	0.000	<b>154.77</b>	91.71

Tracer	Units	Kruskal-Wallis	West mean (no.=13)	East mean (no=19)
Cr <sub>2</sub> O <sub>3</sub>	wt. %	0.011	0.01	0.01
Cs	mg kg <sup>-1</sup>	0.020	<b>4.00</b>	2.87
Cu	"	0.008	<b>35.85</b>	31.32
Dy	"	0.002	<b>11.82</b>	7.66
Er	"	0.006	<b>7.05</b>	4.75
Eu	"	0.001	<b>2.47</b>	1.42
Fe <sub>2</sub> O <sub>3</sub>	wt. %	0.002	<b>5.15</b>	3.64
Ga	mg kg <sup>-1</sup>	0.000	<b>19.65</b>	12.22
Gd	"	0.005	<b>11.52</b>	7.03
Hf	"	0.034	<b>27.39</b>	18.75
Ho	"	0.003	<b>2.40</b>	1.60
K <sub>2</sub> O	wt. %	0.000	<b>2.14</b>	1.28
La	mg kg <sup>-1</sup>	0.002	<b>64.05</b>	40.58
Lu	"	0.002	<b>1.12</b>	0.73
MgO	wt. %	0.002	<b>0.72</b>	0.46
MnO	wt. %	0.048	<b>0.10</b>	0.07
Na <sub>2</sub> O	wt. %	0.015	<b>0.44</b>	0.29
Nb	mg kg <sup>-1</sup>	0.000	<b>25.64</b>	19.74
Nd	"	0.000	<b>62.77</b>	37.95
Ni	"	0.010	<b>20.37</b>	17.54
Pr	"	0.000	<b>16.57</b>	10.14
Rb	"	0.002	<b>91.49</b>	62.03
Se	"	0.023	<b>0.63</b>	0.61
SiO <sub>2</sub>	wt. %	0.001	62.58	<b>72.40</b>
Sm	mg kg <sup>-1</sup>	0.001	<b>13.01</b>	7.67
Sn	"	0.003	<b>4.08</b>	3.16
Ta	"	0.000	<b>2.10</b>	1.49
Tb	"	0.001	<b>2.01</b>	1.26
Th	"	0.002	<b>16.18</b>	11.43
TiO <sub>2</sub>	wt. %	0.001	<b>1.57</b>	1.19
Tl	mg kg <sup>-1</sup>	0.000	<b>0.24</b>	0.12
Tm	"	0.007	<b>1.10</b>	0.74
U	"	0.000	<b>5.87</b>	3.96
V	"	0.001	<b>105.42</b>	78.53
Y	"	0.002	<b>69.74</b>	45.61
Yb	"	0.005	<b>6.82</b>	4.67
Zn	"	0.002	77.31	<b>90.68</b>
Zr	"	0.019	<b>982.98</b>	686.22

Table 3-4: Tracers that differentiate the landscape positions ( $p < 0.05$ ). Bold indicates highest mean concentration.

Tracer (mg kg <sup>-1</sup> )	Units	Kruskal- Wallis	Bank mean (N=18)	Floodplain Mean (N=5)	Point Bar Mean (N=4)	Streets Mean (N=2)	Upland Mean (N=14)
<b>Cu</b>	mg kg <sup>-1</sup>	0.017	39.29	29.28	52.78	<b>88.25</b>	30.57
<b>Dy</b>	mg kg <sup>-1</sup>	0.027	<b>10.51</b>	8.28	10.34	6.58	7.90
<b>Er</b>	mg kg <sup>-1</sup>	0.012	6.42	4.94	<b>6.56</b>	3.82	4.79
<b>Eu</b>	mg kg <sup>-1</sup>	0.025	<b>2.15</b>	1.55	1.80	1.04	1.54
<b>Gd</b>	mg kg <sup>-1</sup>	0.044	<b>10.18</b>	7.71	8.95	5.96	7.38
<b>Hf</b>	mg kg <sup>-1</sup>	0.002	28.13	17.48	<b>38.48</b>	19.60	16.24
<b>Ho</b>	mg kg <sup>-1</sup>	0.005	2.17	1.65	<b>2.29</b>	1.31	1.62
<b>K-40</b>	Bq kg <sup>-1</sup>	0.001	540.62	960.42	<b>1708.16</b>	496.79	991.01
<b>La</b>	mg kg <sup>-1</sup>	0.019	<b>56.57</b>	44.12	46.43	31.30	44.80
<b>Lu</b>	mg kg <sup>-1</sup>	0.039	<b>1.02</b>	0.73	1.08	0.65	0.77
<b>Mo</b>	mg kg <sup>-1</sup>	0.031	1.47	0.86	1.48	<b>2.25</b>	0.81
<b>P<sub>2</sub>O<sub>5</sub></b>	wt. %	0.012	0.12	0.16	0.15	0.29	<b>0.20</b>
<b>Cs-137</b>	Bq kg <sup>-1</sup>	0.001	3.32	<b>27.55</b>	0.86	9.51	18.46
<b>Sn</b>	mg kg <sup>-1</sup>	0.014	3.17	4.00	<b>6.00</b>	5.50	3.64
<b>Tb</b>	mg kg <sup>-1</sup>	0.033	<b>1.76</b>	1.36	1.73	1.02	1.34
<b>TiO<sub>2</sub></b>	wt. %	0.024	1.43	1.15	<b>1.84</b>	1.38	1.16
<b>Tm</b>	mg kg <sup>-1</sup>	0.013	<b>1.02</b>	0.77	1.00	0.61	0.73
<b>Y</b>	mg kg <sup>-1</sup>	0.023	61.54	49.00	<b>67.10</b>	41.00	47.66
<b>Yb</b>	mg kg <sup>-1</sup>	0.007	6.35	4.85	<b>6.56</b>	3.54	4.65
<b>Zr</b>	mg kg <sup>-1</sup>	0.003	983.26	650.92	<b>1491.20</b>	802.60	613.89

#### Suspended Sediment Characterization

The suspended sediment had higher concentrations than the means of the sediment sources by both subwatershed and landscape position in MnO, Cu, Ni, Zn, Cd, Co, Au and Mo (Fig. 3-2). Many of these non-bracketed tracers were of anthropogenic origin; and the sediment sources were primarily characterized by those tracers that are geogenic in origin, not anthropogenic. A missing source of sediment was indicated since the sediment sources did not bracket the suspended sediment. When including as a source a known garbage dump site in a floodplain Zn, Cu, and Au became bracketed, but MnO, Cd, Co, Mo, and Ni remained more concentrated in the suspended sediment than in the sediment sources. Historical photos and materials found at the garbage dump site, such as a pipe with a manufacture date of 1859, indicate when the site was active.

Cu, Mo, and P<sub>2</sub>O<sub>5</sub> were more concentrated in the street residues than in the other landscape positions. The Cu and Mo also were more concentrated in the suspended sediment, and the P<sub>2</sub>O<sub>5</sub> concentration in the street residues approached that found in the suspended sediment. Streets isolate atmospheric particulate matter and channel this flow directly into streams disproportionately to their surface area. Upland soils are a mix of geogenic and anthropogenic elements while streets and other impervious surfaces are direct depositional environments of atmospheric particulate matter. This

suggests that atmospheric particulate matter is a missing sediment source end member.

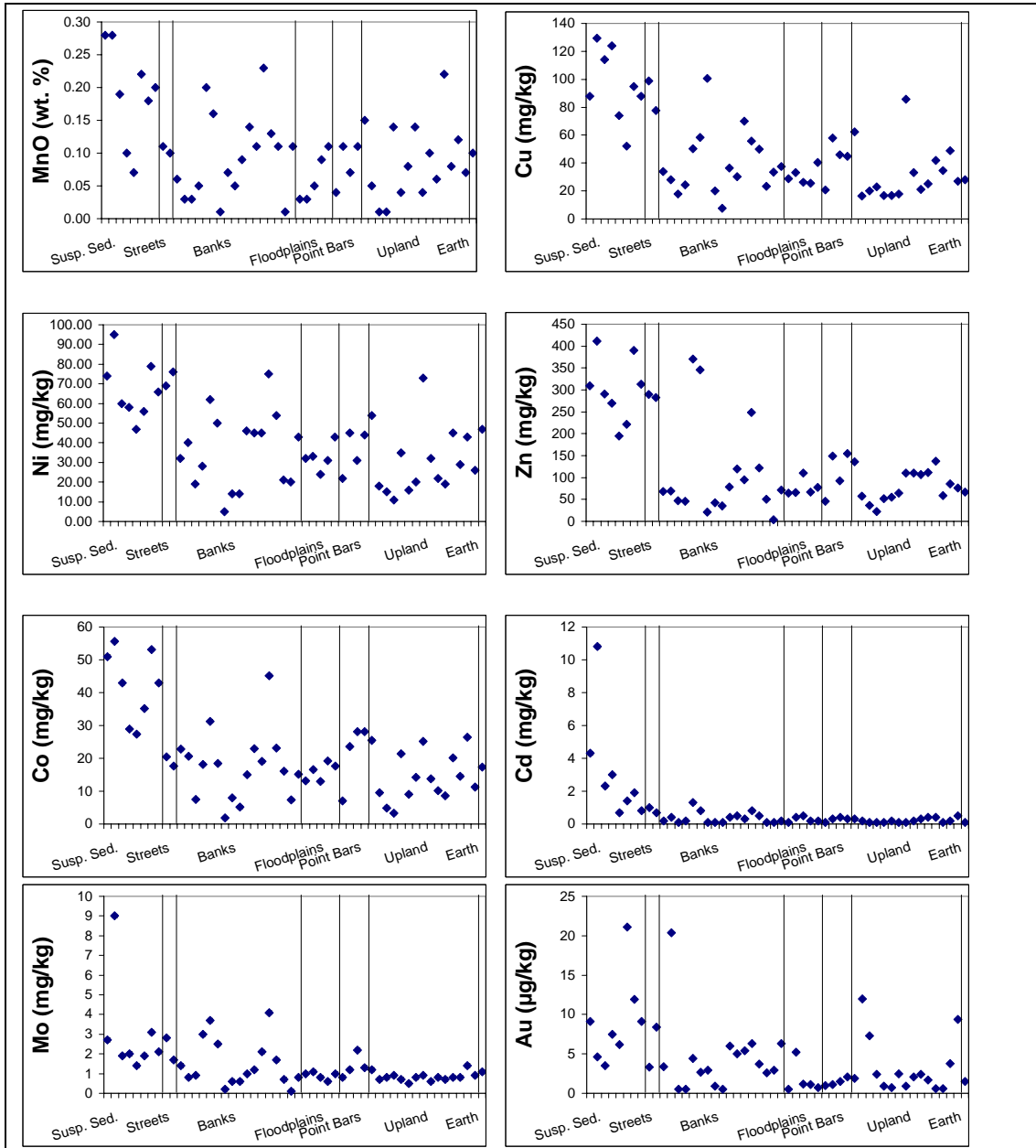


Fig. 3-2: Tracers not bracketed by the sediment sources. The mean concentration in the Earth's upper continental crust is shown for reference (Rudnick and Gao, 2003). The x-axis is landscape position. Measurement error is represented by the size of the point.

The measured concentration of Cu in suspended sediment was similar to Cu concentrations in atmospheric particulate matter collected from two sites in New York (17.00 and 7.30 ng m<sup>-3</sup>/yr), one in New Jersey (4.70 ng m<sup>-3</sup>/yr), several samples from a forested site in Maryland (650 ug/m<sup>2</sup>/yr), and also data on global emissions to

the atmosphere (28,000 metric tons/yr) (Gao et al., 2002; Callender 2004; Scudlark et al., 2005; Almeida et al., 2005; Duan et al., 2006). These studies did not test for Mo or  $P_2O_5$ .

Combined sewer overflows could be an additional source of contamination to the suspended sediment in the stream (Rauter et al., 2005; Tuccillo, 2006). Rainwater enters the sewage pipes from manhole covers adding to the volume of material in the pipes. The high pressure in the sewer pipes during storm events could force sewage out of holes and cracks which otherwise would not leak. Washington Suburban Sanitary Commission reported values of  $61 \text{ mg kg}^{-1}$  dry for Cu and  $5.5 \text{ mg kg}^{-1}$  dry for Mo in lime cake taken from their Parkway processing plant in 2004 (Washington Suburban Sanitary Commission, 2005). This Cu concentration does not approach that in the street residue or suspended sediment samples. This Mo concentration exceeds that found in either street residue or suspended sediment samples. Since Washington Suburban Sanitary Commission measured limed samples, the concentrations are not directly comparable as the sorption of these elements change under different pH levels. Neither sewage nor atmospheric particulate matter was directly sampled as part of this project. However, Washington Suburban Sanitary Commission data indicated that the source of these elements could not be entirely from sewage.

#### Comparison to the Earth's Mean Upper Continental Crust Composition

The trace element concentrations in suspended sediment samples were not bracketed in the sources and were primarily anthropogenic. Therefore the compositions of sediment source groups may not be characterized by anthropogenic trace elements as I originally hypothesized. Tracers that best differentiated sediment sources were geogenic, not anthropogenic. Since the suspended sediment was not bracketed by the sources, a missing source of sediment is suggested—possibly atmospheric particulate matter. While atmospheric particulate matter has an even spatial distribution, the evidence of these particulates is uneven because soils dilute the particulates. Traffic and roads have an uneven spatial distribution that coincides with the undiluted atmospheric particulate matter. Sources may be further parameterized by distinguishing elements that originated from atmospheric particulate matter and/or traffic intensity and road density. This can be done by quantifying the level of trace element enrichment compared to the Earth's mean upper continental crustal composition. If the missing source is of anthropogenic origin, then the tracers for that source will be enriched.

To quantify enrichment of elements compared to the Earth's mean upper continental crustal composition, source samples were compared to the mean composition of the Earth's upper continental crust (Rudnick and Gao, 2003) and normalized to Titanium.  $TiO_2$  had the least variability among the source samples ( $TiO_2$  range = 1.75 wt. %), has chemical stability, and has minor contributions of anthropogenic pollution (Duan et al., 2006). As such  $TiO_2$  is commonly used for normalizations. The following ratio was used:

$$Enrichment\ Factor_{crust,x} = \frac{\left(\frac{x}{y}\right)_{sediment}}{\left(\frac{x}{y}\right)_{crust}} \quad (3-1)$$

Where:

x = concentration of an element

y = concentration of TiO<sub>2</sub>

The source of x is considered anthropogenic where the enrichment factor is greater than 1. To select the most extreme values, only enrichment values > 2 were considered significant. This is an arbitrary threshold and was based on an examination of the data to ensure selectivity of those that are clearly enriched. An example of how this would work is illustrated below.

In a sample, Cd=0.2 mg kg<sup>-1</sup> and TiO<sub>2</sub>=1.24 mg kg<sup>-1</sup>. In the Earth's mean upper continental crustal composition, Cd=0.09 mg kg<sup>-1</sup> and TiO<sub>2</sub>=0.64 mg kg<sup>-1</sup>. The ratio of Cd/ TiO<sub>2</sub> in the sample = 0.16 and the ratio of Cd/ TiO<sub>2</sub> in the Earth's upper crust is 0.14. To determine the level of enrichment, divide the sample by the Earth's upper crust, 0.16/0.14 to get 1.14. Since 1.14 is greater than unity, then Cd is enriched in this sample compared to the Earth's mean upper continental crustal composition.

Of the geogenically derived trace elements, Zr, Pr, Er, and Yb were enriched in the banks located in the west subwatershed. Nd and Hf were enriched in the downstream, mixed portion of the stream banks. No geogenic elements were enriched in the east subwatershed, although Zr and Hf approached the threshold enrichment factor of two. Fig. 3-3 shows elements enriched when comparing subwatersheds plus Nb, Cu, Zn, Sb, Au, Hg, and Pb, which were enriched only in the landscape position comparison.

Of the anthropogenically derived trace elements, Ag and Se were enriched in the east subwatershed. Cd was enriched in the downstream mixed area. This portion of the watershed is highly channelized with cement-lined channels and rock gabions. The primary source of water to the streams in this portion is through storm water drains. Cd, a particulate produced by automobiles (Callender, 2004), is efficiently delivered through these drains as is evidenced by concentrations in the suspended sediment.

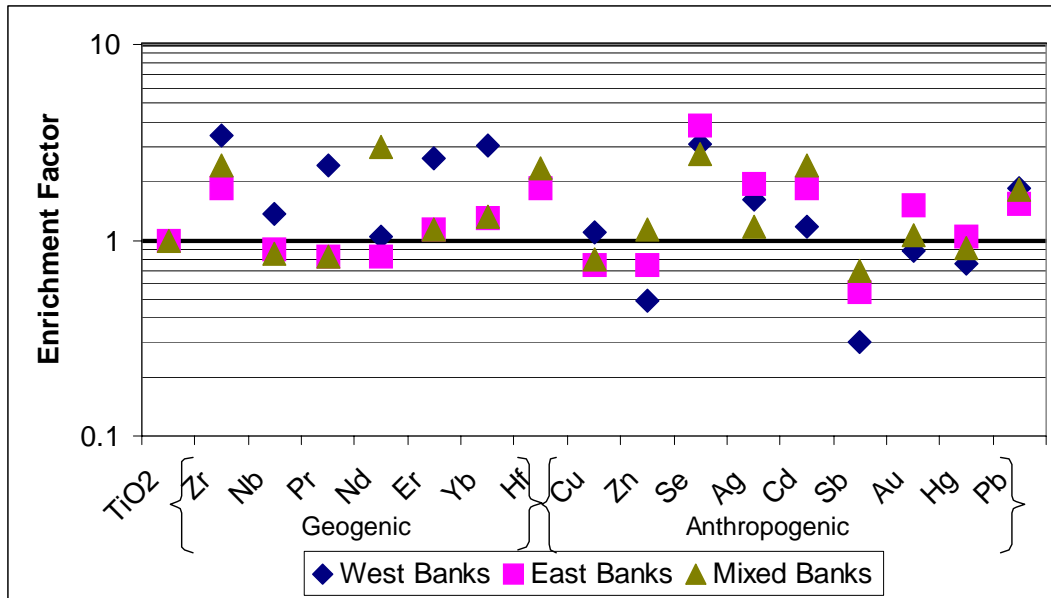


Fig. 3-3 Enrichment of subwatersheds by a factor >2, normalized to Ti.

Fig. 3-4 shows elements enriched when comparing landscape position. The elements Pr and Nd, which were enriched only when comparing subwatersheds, were included for comparison purposes. Of the geogenically derived trace elements, Zr, Er, and Yb were enriched in the stream banks. Nb and Hf are enriched in the point bar samples.

Of the anthropogenically derived trace elements, Cu, Zn, Ag, Au, and Hg were enriched in the suspended sediment samples. Zn is commonly found in very local sources, such as from rusting bridges (M. Goldhaber, personal communication, 2006). The elevated Zn may also reflect a high density of roads since Zn is a component of automobile tires. The Au may be enriched due to the three coal-burning power plants still operating in the region. Coal mined in West Virginia is used in these power plants and has a relatively high concentration of Au compared to other coal sources (M. Goldhaber, personal communication, 2006).

In the floodplain, Se is slightly more enriched than other landscape positions. In the street residue samples Cd, Sb, and Pb are slightly more enriched. The west subwatershed has a higher road density compared to the east subwatershed, which may explain why Pb was the only enriched anthropogenic element in the west. Pb is a product of leaded gasoline widely used until 1978.



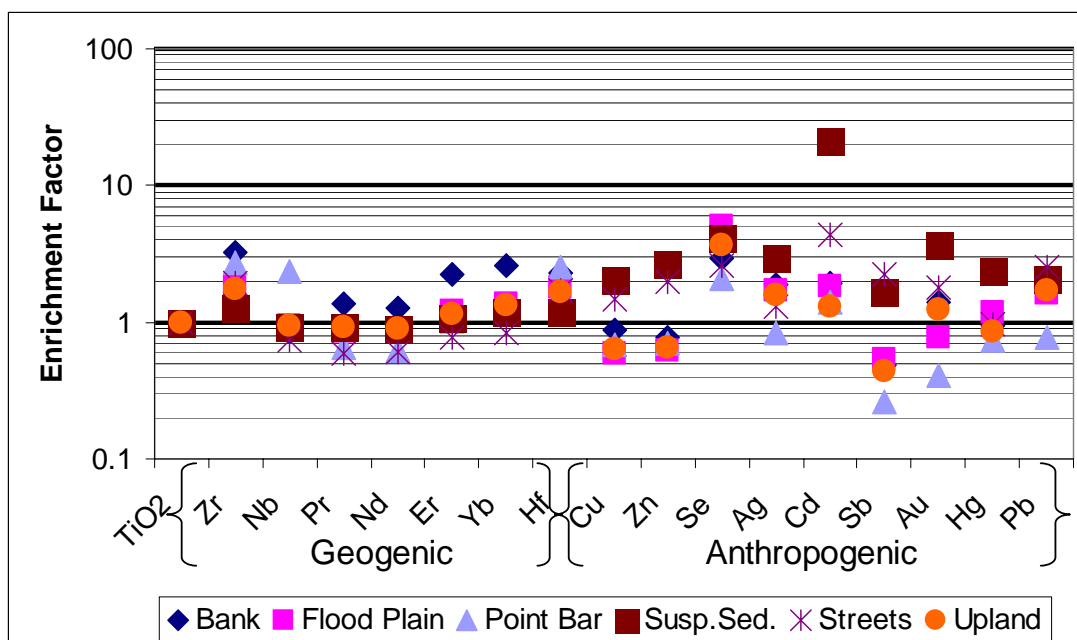


Fig. 3-4 Enrichment of landscape positions by a factor >2, normalized to Ti.

### Discussion

Using an iterative methodology, I tested the sediment fingerprinting method and found geogenic spatial characterizations of sediment sources the best way to group the sediment sources. The use of chemical tracers successfully discriminated sediment sources in this urban watershed. Anthropogenic tracers did not serve as tracers in this study because the suspended sediment samples showed the highest values of these elements; thus they were not bracketed by the sediment source groups. The only two anthropogenic tracers found significant in the landscape position source groupings were Cu and Mo—both elevated in the street residue. The street residue also was enriched in Sb and Pb compared to the mean composition of the Earth's upper continental crust. These elements may not sorb as tightly to particulates at some of the pH values found in this region as do many of the other measured anthropogenic tracers (Impellitteri et al., 2002). Alternatively, they may have been sorbed onto organic matter, which was carried higher in the flow than the suspended sediment sampled in the stream.

Sediment source groups most clearly were defined when element concentrations in the sediment sources were compared to the Earth's upper continental crust. This method discriminated between an overprint on sediment that confounded spatial distribution differences. The non-bracketed suspended sediment and the few significant anthropogenic tracers in the sediment source groups were neither consistent nor easily explained, likely due to a vector of traffic intensity and road density combined with the dilution of atmospheric particulate matter by the soils.

The elements that were *not* enriched compared to the Earth's upper continental crust were primarily of geogenic origin. These included  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,

Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, MnO, Sc, Ba, Be, Co, Cs, Ga, Rb, Sn, Sr, Ta, Th, U, V, W, Y, La, Ce, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Lu, Mo, Ni, As, Bi, and Tl. These trace elements are primarily geogenically derived materials. P<sub>2</sub>O<sub>5</sub>, Ni, As, and Sn being the most notable exceptions. P<sub>2</sub>O<sub>5</sub> is used in fertilizer and may wash off highly fertilized urban yards. Yet, the anthropogenic overprint comprises most of the statistically significant differences between the suspended sediment and sediment sources.

Trace elements that had high concentrations in the suspended sediment were elements commonly associated with anthropogenic origins. The elements with the highest concentrations were Zn, Ba, Zr, and K-40. While the amount of Zr and Ba was high compared to other tracers in the suspended sediment, the concentration was diluted compared to the sediment sources. In contrast, Zn was more highly concentrated in the suspended sediment. Of these four tracers, Zn and Ba are primarily of anthropogenic derivation. K-40 is a natural isotope of K which may come either from the highly micaceous material in the west subwatershed or from fertilizer applied to agricultural crops and urban lawns. Regardless of mass, the tracers of highest concentration in the suspended sediment indicated an anthropogenic imprint.

There were several other elements in the suspended sediment that were not bracketed by the sediment sources but were not enriched compared to the Earth's mean upper continental crustal composition. These included MnO, Ni, Mo, and Co. MnO, Mo, and Co are known to exchange during canopy fall through and in soils (Brady and Weil., 2002; Skudlark et al., 2005).

Atmospheric particulate matter is delivered to impermeable surfaces and washed into the streets and down storm drains. The Washington Sewer and Sanitary Commission also reports a high concentration of Mo (Washington Suburban Sanitary Commission, 2005). Of all of the sources measured, the street residues most closely approached the concentrations found in the suspended sediment. This indicates that the sediment most contaminated by metals is washing off streets and is not coming from point bars, stream banks, or upland areas. Thus, the pathway that delivers the most toxic sediment is one that is only spatially differentiated by measures of impervious surface area and the atmospheric particulate matter that falls on it along with variations in traffic intensity. While the highest mass of eroded material may be coming from banks, floodplains and other soil surfaces, this material is not the most contaminated. Rather the soils dilute the contaminants derived from atmospheric particulate matter and automobile traffic.

The method of calculating enrichment of tracers and comparing to the mean composition of the Earth's upper continental crust provides a concise summary of complex environmental factors. It also helps to explain the origin of the tracers, which provides another tool in teasing apart sources of sediment polluting our waterways.

## Chapter 4: Quantifying Fine Sediment Sources in the Northeast Branch of the Anacostia River

### Introduction

Fine sediment negatively impacts light attenuation in water and diminishes subaquatic vegetation and the benthic biota that depend on vegetation. The EPA has instituted a Total Maximum Daily Load requirement for fine sediment going into the Chesapeake Bay (EPA, 2006c). Determining the sources of fine sediment is relevant to remedying the problem.

The sediment fingerprinting method has been used by researchers extensively (Collins et al., 1997a; Walling and Woodward, 1992; de Boer and Crosby, 1995; Wallbrink et al., 1998; Walling et al., 1999; Rowan et al., 2000; Owens et al., 2000; Jenkins et al., 2002; Carter et al., 2003; Gruszowski et al., 2003; Motha et al., 2003; Papinicolaou et al., 2003; Walling, 2005; Gellis and Landwehr, 2006). This method provides a relative quantification of sediment from various source groups by comparing naturally occurring tracers in sediment sources to suspended sediment. These tracers may be measures of mineral magnetic susceptibility (Slattery et al., 1995), concentrations of radionuclides (Walling and Woodward, 1992; He and Owens, 1995), concentrations of stable isotopes (C-13 and N-15) (Papanicolaou et al., 2003; Gellis and Landwehr, 2006), or concentrations of trace elements (Wallbrink et al., 1998; Motha et al., 2002; Walling, 2005). Depletion or concentration in the elements discriminates between sediment sources.

The sediment fingerprinting approach has primarily been applied in rural settings with land use as the primary classification of source groups and radionuclides used to discriminate sources. Cs-137 was atmospherically deposited 1954-1975 with a significant increase during the year of 1964 as a result of nuclear weapon tests. Surface concentrations of Cs-137 reflect land use, except where mixing or dilution of soils occurred. The highest concentrations of Cs-137 are found in those areas that are undisturbed, such as forested areas, or where soils were translocated from undisturbed areas and not diluted (Nagle and Ritchie 2004, Matisoff et al., 2002; Wallbrink et al. 1998).

In many urban watersheds, urbanization occurs at a variable rate (Jacobson and Coleman, 1986) and does not necessarily occur on continuous plots of land, but rather in small, scattered areas. Therefore, it may be difficult to use land use as a differentiating characteristic of sediment sources in urban areas.

The purpose of this study was to test the sediment fingerprinting approach in an urban watershed. Sources of fine sediment were characterized to determine their sources. Specifically, the hypothesis was: The primary source of suspended sediment in this watershed is derived from stream bank erosion. Knowing the components of suspended sediment samples informed the selection of characteristics for a composite

tracer of source areas. Thus, an iterative process whereby significant characteristics in the suspended sediments were determined at the same time as the measurements in the sediment sources.

### Assumptions

Several assumptions are inherent in sediment fingerprinting research. Suspended sediment samples were only collected during storm events with full aerial extent. If it were to only rain on one portion of the watershed, than that one portion would necessarily be represented in the suspended sediment. It must rain over the entire watershed equally in order to attribute suspended sediment collected downstream to various upstream sources. Gauges were not located in every part of the watershed; however, larger storms that have a broad aerial extent were sampled.

The timing of the sample collection has an impact on the sources identified. Travel times vary according to many factors such as channel roughness and distance from the suspended sediment collection site. If roughness is equal throughout the watershed, then this is not a factor. In terms of travel time, those sources closest to the collection site will be over-represented in samples collected early in the hydrograph. Likewise, headwater sources will be over-represented in samples collected in the falling limb of the hydrograph. The sediment sources attributed to the suspended sediment may not be generalized to the entire storm event, but only to those at the particular point in the hydrograph at which the suspended sample was collected. It is also assumed that all the tracers travel at the same rate. That is, K sorbed onto a particle travels at the same rate as a Si particle. This assumption was not explored as part of this study.

I also assume that the tracers used in this study do not change or participate in any exchange reactions. I assume tracers in the solid phase were not retained or complexed in the soil differently throughout the watershed. I also assume each tracer is equally distributed among the sizes <63  $\mu\text{m}$ , which is the size that remains suspended in the water column (Vanoni, 1975).

### Study Site and Methods

#### Watershed Description

The study site was the Northeast Branch watershed, an 188 km<sup>2</sup> watershed located in an urban area of Maryland near Washington D.C. The watershed spans two physiographic regions—the Piedmont to the west and the Coastal Plain to the East (Fig. 4-1). The Northeast Branch watershed includes two subwatersheds; the western subwatershed is approximately a third the total watershed area and is influenced by Piedmont physiography. The eastern subwatershed is influenced by Coastal Plain physiography. The different geological composition of the two physiographic regions means elemental concentrations are significantly different enough that they may be used as natural tracers.

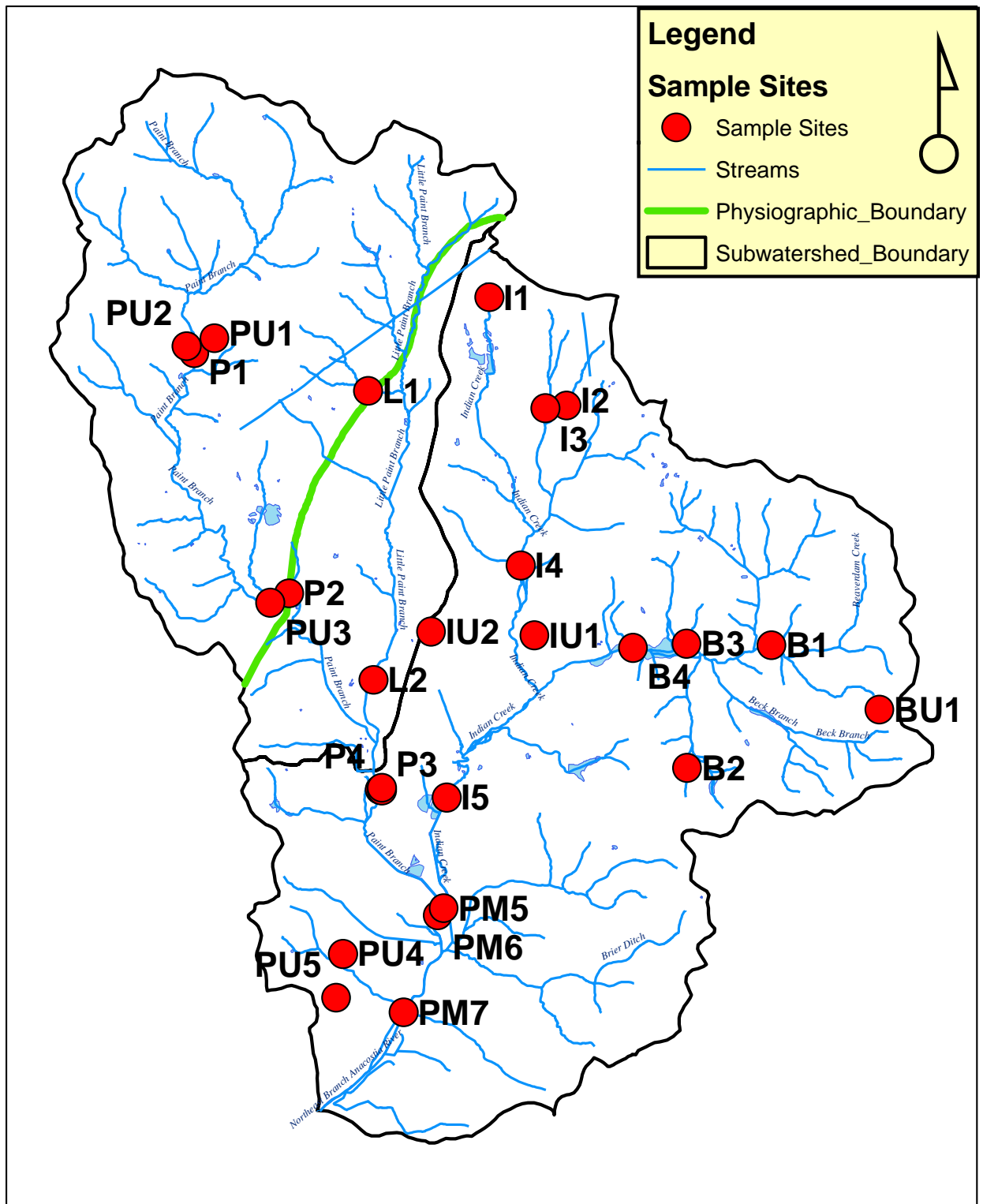


Fig. 4-1 Northeast Branch Watershed sample sites.

There are four streams that drain to the Northeast Branch. From west to east they are: Paint Branch, Little Paint Branch, Indian Creek, and Beaverdam Creek. The confluence of the Paint Branch and Indian Creek forms the Northeast Branch, which drains to the Anacostia River. The Anacostia River in turn drains to the Chesapeake Bay.

The Coastal Plain streams in this study include the entirety of Indian Creek and Beaverdam Creek and the lower portions of Paint Branch and Little Paint Branch. The streams are silt-and clay-bottomed. Sand bars migrate through the two streams that originate in the Piedmont. The Coastal Plain is a low rolling plain. Its geology in this watershed is silt-clay facies of the Potomac Group, comprised of Arundel Clay and much of the lower Patapsco Formation. The Coastal Plain in this area is highly weathered Piedmont material from fluvial deposition. Terrace deposits are the product of stream erosion during the early Quaternary Period. The Coastal Plain sediments range in age from the Cretaceous to Quaternary periods.

Coastal Plain geology primarily comprises silt-clay facies of the Potomac Group (Patuxent Formation), which is Early Cretaceous in age. The Potomac Group is fluvially deposited quartz, with some sandstone and chert. The Coastal Plain also includes Arundel Clay and much of the lower Patapsco Formation. The Coastal Plain in this area is highly-weathered Piedmont material from fluvial deposition. Upland deposits of the Coastal Plain are fluvial sediments of the ancestral Potomac River and are of the late Miocene and Pliocene periods. Terrace deposits are the product of stream erosion during the early Quaternary Period. These are primarily unconsolidated sediments. The Coastal Plain ranges in age from the Cretaceous to Quaternary periods.

The Piedmont streams include the upstream reaches of the Paint Branch and Little Paint Branch and are gravel- and boulder-bedded. Some of the boulders range to several meters in diameter. The floodplains range from three and six meters in width. The region is hilly and slopes are steep and have high elevations. The downstream reaches of these streams are characterized by fewer boulders and more sand.

Mapped units in the Piedmont, including the Laurel formation, are characterized by Precambrian crystalline metamorphic rocks with occasional intrusions of igneous rocks. The granite, gneiss, schist, and other crystalline rocks range in age from Precambrian to late Paleozoic. Piedmont upland deposits are high in vermiculite clay (Glaser, 1996; Csato et al., 2006).

Presently, impervious land in the Anacostia River watershed, which includes the Northeast Branch watershed, is 33% (Maryland Department of Natural Resources, 2000). The Northeast Branch area of the Anacostia is the oldest developed portion of the watershed, developed primarily from between 1960 and 1970. While minor construction projects are currently taking place, there are no current wide-spread Earth-moving projects.

Street residue provides an additional sediment input. Field observation indicates that drainage in decreasing order of magnitude is from storm drains piping runoff from impermeable surfaces directly into the streams, overland flow, and groundwater upwelling. The downstream portions of the streams are channelized with cement, gabions, or granite blocks. The channelization inhibits sediment storage and increases stream flow velocity by decreasing friction.

The Northeast Branch watershed is located between 38° and 39° N and 76° and 77° W. The climate is humid continental with an average temperature of 13.2 °C and an average annual rainfall of 117 cm (NOAA 2005). There are four distinct seasons with mild winters. Rainfall is evenly distributed throughout the year; storms with broad aerial extent occur primarily in winter months. There are isolated thunderstorms in the summer that deliver rain quickly and create flashy stream flow. These summer thunderstorms typically do not span the entire watershed.

### Sampling Strategy

To determine the sources of suspended sediment leaving the Northeast Branch watershed, sites for potential sediment sources were selected at locations throughout the watershed (Fig. 4-1). These sites were located along reaches of each of the four tributaries and the main stem to represent each subwatershed and landscape position of the Northeast Branch Watershed.

The high percentage of impervious surfaces in the watershed resulted in more soil samples from banks, because the paved areas, mostly located in upland areas, could not be sampled. Of the bank samples, there were three sample sites along the Paint Branch, two along the Little Paint Branch, four along Indian Creek, five along Beaverdam, and three along the Northeast Branch. Bank sample sites were chosen at locations where stream width or depth change, topography changes, there was a confluence, or visible erosion was present. These geomorphic changes in the stream areas indicated a possible change in soils and sediments. At five of these stream bank sites, samples were taken along a transect moving away from the bank to include the landscape positions of stream bank, floodplain, and upland. Depending on the topography, the upland position was either a backslope or a summit position. These five sites were selected to represent physiographic region.

The stream banks were defined as those areas immediately adjacent to a stream that contain the stream at average flow. Floodplains were defined as those areas that are broad flatlands on either side of a stream that accommodate maximum flood capacity of a 100-year storm. All other areas were classified as upland.

Sediment source samples were collected from upland soils at 2-5 cm depth of soil with a stainless instrument. Bank samples were collected by scraping away any material plastered from previous stormflow from the bank and vertically integrating the samples. Stream banks in most areas of this watershed were not higher than one meter and were usually shorter.

Street residue was collected for both physiographic regions in the urbanized portions of the watershed. In addition, one construction site located adjacent to a stream and near the suspended sediment collection site was sampled. Street residue was collected by sweeping the street 3.0 meters on either side of a storm drain located on a street adjacent to a stream. Streets were swept with a clean plastic-bristled broom from the center of the street to the curb on both sides of the street (Breault et al., 2005). Street residue samples were collected by aggregating residue from six different streets. To represent seasonal variation, a sample was collected just after leaf fall, in the fall of 2005 and another in the late spring of 2006. The winter was atypically dry with little snowfall, so salt was not broadly applied to streets. Accordingly, a winter sample was not collected.

Four point bars located in the downstream mixed areas of the watershed were also sampled to determine if the bed sediment carried a different chemical signature. Sediment was collected from the top five cm from the upstream end of the bars where the grain size is finer.

Suspended sediment samples were collected in a well-mixed area of the stream just above the U.S. Geological Survey gauge site. The sampling site was upstream of two tributaries that drain into the USGS gauge (Latitude 38°57'36.9", Longitude 76°55'33.5", Fig. 4-1). These tributaries are primarily concrete storm water channels. Because they are concrete channels, the travel time from these areas to the gauge site is less than 0.75 hour on average (K.L. Prestegard, personal communication, 2005). These fluxes would not have been represented in suspended sediment samples because they move through rapidly.

Suspended sediment samples were collected when rainfall covered the entire watershed. Weather forecasts were monitored via the real-time forecasts (Department of Meteorology University of Maryland, NOAA). In addition, a rain gauge eight km from the site was monitored at least three times per day. When rainfall was close to 2.5 cm, the Northeast Branch was visited and assessed for an increase in discharge and sediment movement into the stream. Increased discharge was most likely when the conditions preceding the storm had been wet. Samples were not collected when unsafe conditions existed due to darkness or excessive ice on the roads.

Suspended sediment samples were collected during the rising limb of the hydrograph, which is when the sediment load was most concentrated (Appendix E). An additional sample was collected on April 23, 2006 during the falling limb of the hydrograph.

A flow-proportional method was employed by placing a trash pump into the stream where the current held it above the stream bed but below the surface of the water. Particle sizes <63  $\mu\text{m}$  are well mixed in the water column, so it was not necessary to collect at a particular depth (Vanoni, 1975). The stream water was pumped into three 208-liter steel barrels lined with round-bottomed plastic bags.



Eight suspended sediment samples were collected for the duration of one year to account for seasonal differences in erosion and run-off. The sampling year was July 1, 2005 through June 30, 2006. Collection dates and storm information are in Table 4-1, Fig 4-2, and Appendix E. The fine sediments are on average 25% of the total load carried in the stream. The larger particles do not travel far downstream, but settle out of the water column (Vanoni, 1975).

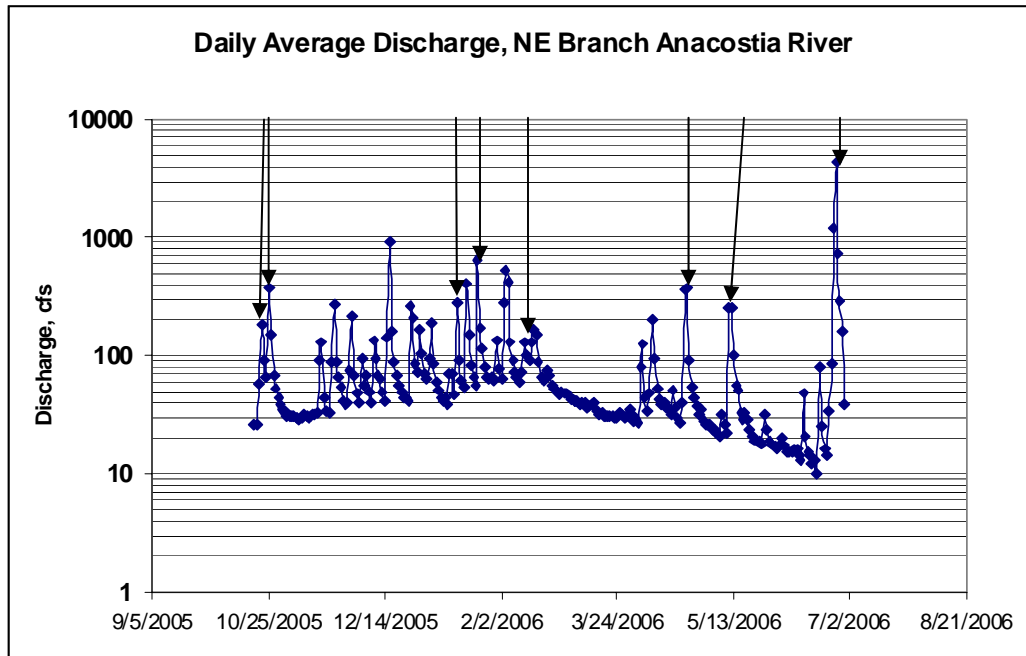


Fig. 4-2: Daily average discharge, Northeast Branch of the Anacostia River. Arrows indicate date suspended sediment sampled.

#### Lab Analyses

##### *Sample Preparation*

Sediment source samples were air-dried in an isolated lab to decrease the potential of cross-contamination. Visible leaves, twigs, and garbage in the samples were removed manually. Each sample was ground with a mortar and pestle and sieved to  $<63 \mu\text{m}$  using a shaker.

Suspended sediment samples were prepared by removing the stream water from the barrels within one week following collection. A Teflon-lined continuous centrifuge was used for sediment removal. The centrifuge was selected because the Teflon lining would prevent metal contamination from the machine itself. Suspended sediment samples were dried in an oven at  $60^\circ \text{C}$ . The suspended sediment samples were also ground and dry-sieved to  $<63 \mu\text{m}$  using a shaker.

Organic matter was not removed from any of the samples prior to radionuclide analysis. Organic matter differences are complex and difficult to generalize, therefore even where significant organic matter is present, corrections are frequently not made (Walling, 2005). The sample preparation process for the elemental analysis by ICP

includes dissolution by  $\text{HNO}_3$ . This dissolution oxidizes the organic matter and leaves the metals as residuals. This yields the total elemental load for this size class, but does not discriminate among the metals sorbed to organic versus inorganic sediment (Sun et al., 2001; Impellitteri et al., 2002). In all of the source samples, total carbon was < 9.9%.

Table 4-1: Suspended sediment sample characteristics. \*\*at last available time before gauge failed.

Date and time of suspended sediment collection	Q at time of suspended sediment collection ( $\text{m}^3 \text{s}^{-1}$ )	Date and time of hydrograph peak	Q at hydrograph peak ( $\text{m}^3 \text{s}^{-1}$ )	Sediment collected ( $\text{g m}^{-3}$ )	<0.63 $\mu\text{m}$ Sediment ( $\text{g m}^{-3}$ )	<0.63 $\mu\text{m}$ sediment/bulk sediment collected	Sediment flux at time collected ( $\text{g s}^{-1}$ , <0.63 $\mu\text{m}$ )
10/7/2005 at 12:30	15.51	10/8, at 7:00	55.87	23.05	8.21	36%	127.37
10/22/2005 at 9:00	0.83	10/22 at 9:30	2.16	250.72	53.76	21%	44.67
12/25/2005 at 15:00	0.33	12/25 at 18.15	3.32	105.46	31.57	30%	10.52
1/18/2006 at 9:00	4.00	1/18 at 11:45	10.55	175.12	37.56	21%	150.15
2/4/2006 at 16:00	0.80	2/4 at 21:00	6.61	120.7	31.99	27%	25.58
4/23/2006 at 6:05	1.46	4/22 at 21:00	9.09	623.46	199.33	32%	290.63
5/11/2006 at 20:30	0.39	5/11 at 21:00	4.24	114.2	15.914	14%	6.24
6/25/2006 at 11:45	14.39	6/25 at 20:30 **	173.72**	293.09	62.23	21%	31613.37

### ***Radionuclides***

Radionuclide analysis was performed on sediment source samples and suspended sediment samples by gamma-ray spectrometry using a Canberra-2000 Genie-2000 Spectroscopy System for 24 hours. The long duration of the spectrometry allows lower concentrations to be detected. The system was calibrated and efficiency determined using an analytic mixed radionuclide standard; the calibrations are traced to the U.S. National Institute of Standards and Technology.

### ***Elemental analysis by ICP-MS and ICP-ES***

The elemental analysis was performed by Acme Analytical Laboratories Ltd. ICP-emission spectrometry was performed following a  $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$  fusion at  $980^\circ\text{C}$  and dissolution in 0.5%  $\text{HNO}_3$ . The  $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$  fusion process lowers the boiling point allowing for more complete dissolution. Rare Earth and refractory elements were tested by ICP-mass spectrometry following the same fusion and dissolution process. Total carbon and sulfur were determined by LECO. Loss on ignition (LOI)

was determined by weight difference after ignition at 1000°C. The elements and method for each are in Table 4-2.

A sample-prep blank was carried through all stages of preparation and analysis as the first sample. Two reagent blanks measured background. Standard reference materials prepared by Acme using internationally certified reference materials were used to monitor accuracy. Maximum acceptable error for precision and accuracy was  $\pm 5\%$  at concentrations  $>100\times$  the detection limit (Appendix D).

Table 4-2: Element analytical methods

Method	Chemical Tracer
LiBO <sub>2</sub> /Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> fusion analysis by ICP-ES.	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , MgO, CaO, Na <sub>2</sub> O, K <sub>2</sub> O, TiO <sub>2</sub> , P <sub>2</sub> O <sub>5</sub> , MnO, Cr <sub>2</sub> O <sub>3</sub> , Ni, and Sc
LECO	Total C, Total S
Rare Earth and Refractory Elements: LiBO <sub>2</sub> /Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> fusion analysis by ICP-MS	Ba, Be, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W, Zr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
Leach with 3 ml 2-2-2 HCl-HNO <sub>3</sub> -H <sub>2</sub> O (aqua regia) at 95°C for 1 hour, diluted to 10 ml, analyzed by ICP-MS.	Mo, Cu, Pb, Zn, Ni, As, Cd, Sb, Bi, Ag, Au, Hg, Tl, Se

### ***Sediment Source Identification***

Tracer concentrations were examined for normality using SAS v. 9.1 (SAS Institute Inc., 2004). Unequal variances were evident from the probability plot and box plots. Normality was violated, so non-parametric tests were used. In addition, there were orders of magnitude differences between the tracers and ranking the data allowed for clearer comparison.

Source groups were determined based on a Spearman-correlation matrix of elemental and radionuclide concentrations. In addition, the landscape model derived from a soil survey (Appendix A) helped to inform the grouping of sediment sources. The sources of fine sediment in the Northeast Branch watershed were grouped in two ways—by subwatershed and landscape position. Each source grouping and subsequent comparison with suspended sediment was considered separately.

Those tracers that were more enriched in the sediment source samples than in the mean composition of the Earth's upper continental crust were removed following procedures outlined in a companion study (Chapter 3). The tracers were removed because some did not vary on a spatial pattern and others did not bracket the suspended sediment. Those that did not vary on a spatial pattern included: Hg, Pb, Ag, Se, Hf, Yb, Er, Nd, Pr, Nb, Zr, and Sb. Removing these enabled focus on the parameters that best described the sediment sources on a spatial basis. Those tracers in the suspended sediment whose concentrations were not bracketed by the sediment source areas were an indication of a missing source of sediment. These tracers were largely from atmospheric particulate matter (Chapter 3). Street residue concentrations

approached concentrations measured in the suspended sediment, but were not always greater than the suspended sediment. I discarded these tracers from statistical consideration. The tracers that were removed because the tracer concentrations were higher in the suspended sediment than in the sources identified for this study included: MnO, Cu, Zn, Co, Ni, As, Cd, and Au. Those that are bracketed are shown in Table 4-3.

Table 4-3: Bracketed Tracers

Tracer	Units	Sediment Sources				Suspended Sediment			
		Mean	Sample Variance	Min.	Max.	Mean	Sample Variance	Min.	Max.
Cs-137	Bq/kg	15.34	330.62	0.00	61.11	3.55	5.56	0.00	6.09
K-40	Bq/kg	760.47	288315.30	4.26	2342.38	1315.55	596058.68	118.30	2660.29
SiO <sub>2</sub>	%	72.11	47.74	56.27	78.94	63.59	9.99	59.09	70.32
Al <sub>2</sub> O <sub>3</sub>	%	9.93	10.06	6.45	19.33	12.28	2.72	10.08	14.52
Fe <sub>2</sub> O <sub>3</sub>	%	3.74	0.76	2.84	5.70	5.66	0.27	4.75	6.36
MgO	%	0.40	0.02	0.20	0.65	1.03	0.05	0.77	1.47
CaO	%	0.26	0.03	0.03	0.70	0.83	0.12	0.50	1.65
Na <sub>2</sub> O	%	0.27	0.01	0.14	0.45	0.31	0.00	0.26	0.38
K <sub>2</sub> O	%	1.27	0.06	0.80	1.68	1.50	0.03	1.28	1.80
TiO <sub>2</sub>	%	1.19	0.13	0.91	2.39	1.08	0.01	0.95	1.16
P <sub>2</sub> O <sub>5</sub>	%	0.14	0.00	0.07	0.29	0.24	0.00	0.16	0.32
MnO	%	0.05	0.00	0.01	0.14	0.19	0.01	0.07	0.28
Cr <sub>2</sub> O <sub>3</sub>	%	0.01	0.00	0.01	0.02	0.02	0.00	0.01	0.02
Ni	mg/kg	25.00	137.38	5.00	45.00	66.88	232.70	47.00	95.00
Sc	mg/kg	10.43	5.80	8.00	17.00	13.13	1.55	12.00	15.00
LOI	%	10.47	27.95	5.90	22.30	13.11	4.93	10.30	17.60
Total C	%	3.00	5.58	0.13	7.73	4.11	1.63	3.08	6.73
Total S	%	0.04	0.00	0.01	0.12	0.09	0.00	0.05	0.19
Sum	%	99.85	0.03	99.38	99.98	99.85	0.00	99.73	99.92
Ba	mg/kg	294.72	3132.50	184.70	377.80	342.81	2849.48	288.00	430.50
Be	mg/kg	1.79	0.95	1.00	4.00	2.25	0.21	2.00	3.00
Co	mg/kg	13.60	58.67	1.80	23.60	42.11	117.80	27.30	55.60
Cs	mg/kg	2.94	0.87	1.80	4.90	3.54	0.13	3.10	4.10
Ga	mg/kg	12.59	12.16	8.10	21.20	16.11	4.44	12.90	18.50
Hf	mg/kg	18.89	147.52	5.20	55.60	10.63	3.64	7.70	14.20
Nb	mg/kg	19.86	11.61	16.50	29.70	18.44	1.91	16.10	20.00
Rb	mg/kg	61.29	175.08	37.40	82.90	74.58	48.13	64.40	86.20
Sn	mg/kg	3.07	1.76	2.00	6.00	4.75	0.50	4.00	6.00
Sr	mg/kg	53.54	48.00	40.30	62.70	66.13	4.01	63.00	69.10
Ta	mg/kg	1.54	0.06	1.10	2.20	1.33	0.02	1.20	1.50
Th	mg/kg	11.59	5.30	9.30	17.10	10.13	1.01	8.70	11.40
U	mg/kg	3.96	0.71	2.70	6.50	3.54	0.04	3.30	3.90
V	mg/kg	81.29	353.30	56.00	129.00	105.38	59.13	93.00	119.00
W	mg/kg	1.94	0.07	1.50	2.40	1.98	0.08	1.70	2.50
Zr	mg/kg	691.31	230242.12	211.00	2182.40	413.73	5259.05	301.40	545.50
Y	mg/kg	46.70	112.46	32.40	76.10	43.88	4.03	40.50	46.40

Tracer	Units	Sediment Sources				Suspended Sediment			
		Mean	Sample Variance	Min.	Max.	Mean	Sample Variance	Min.	Max.
La	mg/kg	40.56	34.63	29.30	51.00	40.21	19.86	34.80	49.80
Ce	mg/kg	90.89	247.59	64.30	127.40	98.60	73.82	87.70	112.20
Pr	mg/kg	10.01	3.30	7.14	14.33	11.09	0.92	9.93	12.56
Nd	mg/kg	37.14	43.92	24.90	49.80	40.96	18.86	35.90	49.30
Sm	mg/kg	7.66	2.23	5.10	9.70	8.58	0.41	7.80	9.80
Eu	mg/kg	1.44	0.09	0.85	1.83	1.55	0.03	1.38	1.86
Gd	mg/kg	7.13	2.10	4.40	9.78	7.42	0.41	6.52	8.56
Tb	mg/kg	1.27	0.07	0.85	1.93	1.31	0.01	1.17	1.43
Dy	mg/kg	7.82	1.98	5.33	11.17	7.53	0.19	6.79	7.99
Ho	mg/kg	1.62	0.13	1.16	2.67	1.48	0.00	1.35	1.55
Er	mg/kg	4.88	1.20	3.64	7.79	4.15	0.09	3.78	4.81
Tm	mg/kg	0.75	0.03	0.54	1.20	0.63	0.01	0.55	0.77
Yb	mg/kg	4.79	1.32	3.43	7.85	3.88	0.11	3.41	4.48
Lu	mg/kg	0.75	0.04	0.47	1.32	0.63	0.00	0.58	0.66
Mo	mg/kg	0.98	0.42	0.20	3.00	3.01	6.13	1.40	9.00
Cu	mg/kg	31.70	505.17	16.50	100.50	95.53	683.00	52.10	129.50
Pb	mg/kg	31.15	315.76	5.80	70.70	58.65	73.47	46.20	70.00
Zn	mg/kg	60.86	1149.52	21.00	149.00	299.88	5576.13	194.00	411.00
Ni	mg/kg	15.36	59.30	2.60	30.70	48.16	196.58	30.70	75.10
As	mg/kg	4.48	1.68	3.00	7.00	5.90	0.43	4.90	7.20
Cd	mg/kg	0.21	0.02	0.10	0.50	3.15	10.96	0.70	10.80
Sb	mg/kg	0.31	0.03	0.10	0.60	1.10	0.18	0.40	1.90
Bi	mg/kg	0.16	0.00	0.10	0.20	0.29	0.01	0.20	0.50
Ag	mg/kg	0.15	0.02	0.10	0.60	0.26	0.01	0.10	0.40
Au	µg/kg	4.27	32.06	0.50	20.40	9.13	30.63	3.50	21.10
Hg	mg/kg	0.08	0.00	0.03	0.25	0.20	0.00	0.12	0.28
Tl	mg/kg	0.11	0.00	0.10	0.20	0.19	0.00	0.10	0.20
Se	mg/kg	0.59	0.04	0.50	1.20	0.63	0.01	0.50	0.70

The non-parametric Kruskal-Wallis means comparison test was used to identify the remaining tracers with significant differences between source groups. Tracers that failed this test ( $p < 0.05$ ) were removed. The Mann-Whitney test, which is a non-parametric means comparison test between two variables, was used to compare sediment source groups on a pair-wise basis. Sediment source groups that showed no significant differences in this test were eliminated.

Others have successfully used discriminant function analysis to further discriminate which of the tracers are significant between each of the source groups (Owens et al., 2000; Walling, 2005). It was not an option in this study because the data violated four of the five assumptions of discriminant function analysis: 1) normality, 2) no outliers, 3) homoscedasticity, 4) no skewness, 5) no multi-collinearity (Poulson and French, 2006). Many of the tracers were highly correlated with each other, as would be expected with the elements that make up the minerals in the sediment. In addition, there were several outliers, presumably from specific outcroppings of a unique

geologic material or of a point-source pollutant. These outliers impact the mean and increase variability. Thus, the pooled variances result in erroneous statistical significance. The data also does not have homoscedascity. This could affect within-group variations of the source groups. Lastly, the data was not normally distributed, which was caused by skewness and outliers. In lieu of discriminant function analysis to determine between group variations, I used Mann-Whitney and tested the differences in tracers in each pair of sources.

Once the tracers identifying each source group were statistically verified, a mixing model was used to attribute relative quantities of suspended sediment to sources for a particular storm event. Mixing models have been used in groundwater research for decades when looking for sources in aquifers. In sediment fingerprinting, various mixing models have been used (Rowan et al., 2000; Collins et al., 1997b; Walling et al., 1999). The model I used was developed specifically for small sample sizes (Gellis and Landwehr, 2006). The model solves the system of linear equations whereby the sum of the source contributions equals unity and the standard deviation of the tracer properties in the suspended sediment are related to the source group. The source contributions account for the unknown proportion of contributions of each source group. The function was minimized by the root mean square of the variance of the tracers in the source groups. The error term is a standard deviation; therefore the tracers are normalized in the mixing model. Each source and tracer is scaled by the standard deviation of the mixture so that they are comparable. This model is unique because it is based on normalizing a standard deviation of a mixture as opposed to directly relating the values of each variable; thereby giving this model more statistical power (J.M. Landwehr, personal communication, 2006). Tracers which approach zero concentration may be used because the formula is a standard deviation and does not depend on dividing directly by the tracer concentration. This is particularly useful when using elemental tracers that are commonly found in very low concentrations.

$$E = \left( \frac{1}{T} \right) \sum_{t=1}^T \frac{\left| \left\{ V_t - \sum_{s=1}^S f_s A_{st} \right\} \right|}{\sqrt{\left\{ \sum_{s=1}^S f_s^2 VAR_{st} \right\}}} \quad (4-1)$$

Where:

T=total no. of tracers

t=a specific tracer

V<sub>t</sub>=value of the tracer t in the suspended sediment

f<sub>s</sub>=fractional sources, must sum to one

S=total no. of source groups

s=source group

A<sub>st</sub>=average of a specific tracer (t) in the source group (s)

VAR<sub>st</sub>= variance of a specific tracer (t) in the source group (s)

With three source groups, the same error value can be generated by a variety of different parameter combinations. This indicates that a single optimized solution is only one of many statistically equivalent solutions that each may yield different results in terms of source contribution (Rowan et al., 2000). Some of the sources necessarily have a greater degree of sensitivity. This may be caused by the tracers used to identify this source group or by a higher number of samples in a particular source group. Thus, the optimal model is only one of many outcomes that have a small error. Since the model can have the same optimization, it was necessary to compare the different explanations and use the explanation that makes the most sense given the study site (Owens et al., 2000). Propagating all uncertainties to the final source contribution could be achieved through a Bayesian Monte Carlo simulation approach (Rowan et al., 2000). However, that is outside the scope of this project. In lieu of additional statistical tests, results were compared with the landscape model, developed during a soil survey (Chapter 2). This landscape model provided information about erodibility mechanisms such as mass wasting, soil structure, particle size differences, and channel roughness. The source contributions with minimum error matched predictions from the landscape model.

## Results

### Suspended Sediment Characterization

The elemental concentrations in the suspended sediment are shown in Table 4-4. The suspended sediment collected during storm events was most concentrated in anthropogenic elements. The most variation in suspended sediment between storm events was in Cd.

Table 4-4: Elemental concentrations in suspended sediment.

Trace Elements	Units	Mean	STD	CV	Min	Max
<b>Sc</b>	mg kg <sup>-1</sup>	13.13	1.25	9.50	12.00	15.00
<b>Total S</b>	wt. %	0.09	0.05	54.02	0.05	0.19
<b>Ba</b>	mg kg <sup>-1</sup>	342.81	53.38	15.57	288.00	430.50
<b>Be</b>	"	2.25	0.46	20.57	2.00	3.00
<b>Co</b>	"	42.11	10.85	25.77	27.30	55.60
<b>Cs</b>	"	3.54	0.36	10.13	3.10	4.10
<b>Ga</b>	"	16.11	2.11	13.08	12.90	18.50
<b>Hf</b>	"	10.63	1.91	17.95	7.70	14.20
<b>Nb</b>	"	18.44	1.38	7.50	16.10	20.00
<b>Rb</b>	"	74.58	6.94	9.30	64.40	86.20
<b>Sn</b>	"	4.75	0.71	14.89	4.00	6.00
<b>Sr</b>	"	66.13	2.00	3.03	63.00	69.10
<b>Ta</b>	"	1.33	0.13	9.67	1.20	1.50
<b>Th</b>	"	10.13	1.00	9.92	8.70	11.40
<b>U</b>	"	3.54	0.19	5.43	3.30	3.90
<b>V</b>	"	105.38	7.69	7.30	93.00	119.00

Trace Elements	Units	Mean	STD	CV	Min	Max
W	"	1.98	0.28	14.00	1.70	2.50
Zr	"	413.73	72.52	17.53	301.40	545.50
Y	"	43.88	2.01	4.58	40.50	46.40
La	"	40.21	4.46	11.08	34.80	49.80
Ce	"	98.60	8.59	8.71	87.70	112.20
Pr	"	11.09	0.96	8.66	9.93	12.56
Nd	"	40.96	4.34	10.60	35.90	49.30
Sm	"	8.58	0.64	7.50	7.80	9.80
Eu	"	1.55	0.16	10.19	1.38	1.86
Gd	"	7.42	0.64	8.65	6.52	8.56
Tb	"	1.31	0.09	6.53	1.17	1.43
Dy	"	7.53	0.44	5.82	6.79	7.99
Ho	"	1.48	0.07	4.57	1.35	1.55
Er	"	4.15	0.30	7.25	3.78	4.81
Tm	"	0.63	0.07	11.48	0.55	0.77
Yb	"	3.88	0.34	8.70	3.41	4.48
Lu	"	0.63	0.03	4.36	0.58	0.66
Mo	"	3.01	2.48	82.17	1.40	9.00
Cu	"	95.53	26.13	27.36	52.10	129.50
Pb	"	58.65	8.57	14.61	46.20	70.00
Zn	"	299.88	74.67	24.90	194.00	411.00
Ni	"	48.16	14.02	29.11	30.70	75.10
As	"	5.90	0.65	11.06	4.90	7.20
Cd	"	3.15	3.31	105.11	0.70	10.80
Sb	"	1.10	0.43	38.87	0.40	1.90
Bi	"	0.29	0.10	34.47	0.20	0.50
Ag	"	0.26	0.12	45.25	0.10	0.40
Au	"	9.13	5.53	60.65	3.50	21.10
Hg	"	0.20	0.06	29.07	0.12	0.28
Tl	"	0.19	0.04	18.86	0.10	0.20
Se	"	0.63	0.07	11.31	0.50	0.70

Minor Elements	Units	Mean	STD	CV	Min	Max
Na <sub>2</sub> O	wt. %	0.31	0.04	14.21	0.26	0.38
MnO	"	0.19	0.08	39.69	0.07	0.28
Cr <sub>2</sub> O <sub>3</sub>	"	0.02	0.00	20.16	0.01	0.02

Major Elements	Units	Mean	STD	CV	Min	Max
SiO <sub>2</sub>	wt. %	63.59	3.16	4.97	59.09	70.32
Al <sub>2</sub> O <sub>3</sub>	"	12.28	1.65	13.43	10.08	14.52
K <sub>2</sub> O	"	1.50	0.17	11.51	1.28	1.80
Fe <sub>2</sub> O <sub>3</sub>	"	5.66	0.52	9.19	4.75	6.36
MgO	"	1.03	0.21	20.67	0.77	1.47
CaO	"	0.83	0.35	41.86	0.50	1.65
TiO <sub>2</sub>	"	1.08	0.08	7.07	0.95	1.16
LOI	"	13.11	2.22	16.93	10.30	17.60



Radionuclide Isotopes	Units	Mean	STD	CV	Min	Max
Cs-137	Bq kg <sup>-1</sup>	3.55	2.36	66.46	0.00	6.09
K-40	Bq kg <sup>-1</sup>	1315.55	772.05	58.69	118.30	2660.29

#### Sediment Source Group Characterization

##### *Source Groups: East and West Subwatershed*

Those tracers that were not significant at  $p < 0.05$  in the Mann-Whitney test were the two radionuclides, Cs-137 and K-40, as well as  $P_2O_5$ , CaO, Sr, W, and Mo. These were removed from further consideration, in addition to the anthropogenically enriched elements discussed in Chapter 3. The downstream portions of the Northeast Branch watershed, where the west and east subwatersheds mix, were not considered in the Mann-Whitney test. The mixed portion of the watershed is not an end-member and therefore sediment source can not be ascribed to the mixed portion using a mixing model.

Several of the significant tracers covaried (Fig. 4-3). To strengthen the model, elements were selected that were neither highly correlated nor necessarily coexist with one another because of chemical properties. Tracers with the lowest p-value were selected from different groups of the periodic table, e.g.: one element from the lanthanides and one from the alkali Earth metals (Appendix H). When there was more than one element in a group with a very low p-value, the tracer with the largest atomic radius, lowest ionic potential, and lowest electron affinity was selected. The tracers that were selected based on these criteria included Ga, Ta, Ce, and U (Table 4-5). None of these four elements naturally bind with one another and all are stable in the environment. Each was graphed against the other and none co-varied.

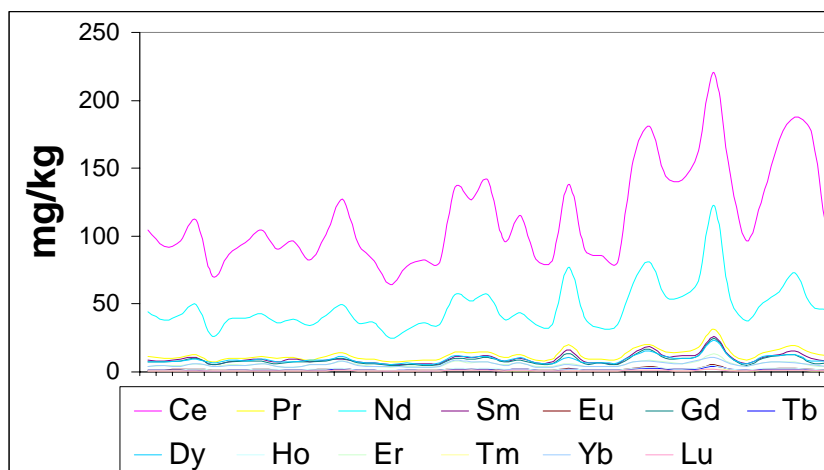


Fig. 4-3: Covariance between tracers in the Lanthanide Group. X-axis is sample.

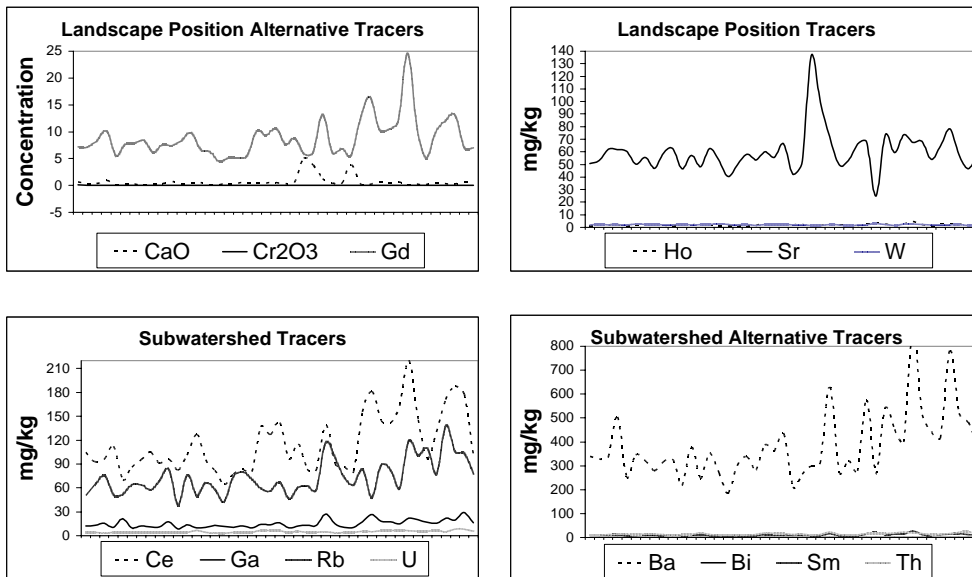


Fig: 4-4: Covariance between tracers used in the mixing model. X-axis is sample.

Table 4-5: Tracers that Differentiate Sediment Sources by Hydrological Subwatershed Boundary

Tracer	Kruskal-Wallis	West Mean (N=10)	West CV (N=10)	East mean (N=15)	East CV (N=15)	Periodic Group
Ce ( $\text{mg kg}^{-1}$ )	0.000	<b>163.98</b>	19.88	89.02	14.81	Lanthanide
Ga ( $\text{mg kg}^{-1}$ )	0.012	<b>20.27</b>	22.97	12.24	23.72	Metal
Ta ( $\text{mg kg}^{-1}$ )	0.000	<b>2.11</b>	12.19	1.47	11.61	Transition metal
U ( $\text{mg kg}^{-1}$ )	0.000	<b>5.99</b>	20.78	3.85	10.89	Actinide

Results of the mixing model that was used to determine the relative quantity of fine sediment attributable to each source indicate that storm events varied considerably according to season, rainfall intensity and rainfall volume (Table 4-6). Suspended sediment was attributable to the east subwatershed for all events except the October 22, 2005 storm event and the February 9, 2006 storm event. In the October 22, 2005 storm event, the rainfall volume was low and a 200-year storm had occurred two weeks prior. The February 9, 2006 storm event is the only event sampled where there had been sizeable rainfall and runoff within the previous 24 hours. Both the October 22 and February 9 event had suspended sediment that could be attributed to the west subwatershed.

Travel paths are further from the west to the gauge than from the east to the gauge. Sediment measured at a particular point in the hydrograph may represent a sample based more on travel time than a preference for either subwatershed to contribute fine sediment. Since the two events contributing suspended sediment from the west had preceding conditions that moved sediment, it is possible that sediment in temporary storage only made it to the gauge in time for sampling with the addition of a

subsequent storm event. Without the subsequently sampled storm, the west suspended sediment would move through during the falling limb of the hydrograph.

Table 4-6: Estimation of Relative Sediment Source Contributions by Hydrological Subwatershed using tracers Gallium, Tantalum, Cerium, and Uranium.

Suspended Sediment	West	West Flux	East	East Flux	Error
Date	% Contributing	(g/s)	% Contributing	(g/s)	
10/7/2005	0%	0.00	100%	127.37	0.377
10/22/2005	31%	13.80	69%	30.86	0.748
12/25/2005	0%	0.00	100%	10.52	0.661
1/18/2006	0%	0.00	100%	150.15	0.957
2/4/2006	5%	1.30	95%	24.28	0.213
4/23/2006	0%	0.00	100%	290.63	0.784
5/11/2006	0%	0.00	100%	6.24	0.676
6/25/2006	0%	0.00	100%	31613.37	0.729
average	5%	1.89	96%	4031.68	0.643
fall average	16%	6.90	85%	79.12	0.563
winter average	2%	0.43	98%	61.65	0.61
spring average	0%	0.00	100%	10636.75	0.73

#### ***Source Groups: Landscape Position***

The Kruskal-Wallis test performed on point bars, banks, floodplains, upland areas, and street residue identified 18 significant tracers. Non-significant tracers, including SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, Sn, Na<sub>2</sub>O, K<sub>2</sub>O, Ba, Be, Cs, Ga, Nb, Rb, Mo, Ta, Th, U, V, Ce, Bi, and Tl, were removed from further analysis.

A pair-wise comparison of source groups using the Mann-Whitney test showed no tracers were found significantly different between the floodplain and the streets or the floodplain and the upland areas. Only one tracer was found in a significantly different concentration between the floodplains and the banks—Cs-137. A floodplain is similar to a bank since it includes the gradual addition of the same sediments that form a bank. Therefore, floodplains were not considered as a separate source group.

The Mann-Whitney test identified only one tracer as significantly different between point bars and streets—Cs-137. Point bars are made up of stream bed material, which is temporary storage of sediment. This source group is also confounded by an overall larger particle size (Appendix F). Sieving the point bars to the <0.63 µm particle size did result in enough sample for analysis, but the mean particle-size of the point bars was much higher than in any other sample. Therefore, point bars could not be considered comparable independent sources and were not considered as a separate source group.

The source groups that were possible to discriminate, and therefore available to attribute suspended sediment to, were the banks, upland, and street residue landscape positions. The tracers that were significant when comparing the bank and upland were: Cs-137, K-40, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Y, La, Eu, Gd, Tb, Dy, Ho, Tm, Lu, and Sm. The tracers that significantly differentiated the bank from the street residue were: P<sub>2</sub>O<sub>5</sub>, La, Eu, Tb, Dy, Ho, Tm, CaO, Sm, Sr, and W. The tracers that differentiated the upland from the streets were CaO, Cr<sub>2</sub>O<sub>3</sub>, Sr, and W.

To eliminate multi-collinearity and to ensure that at least one tracer uniquely separated each of the three source groups, I narrowed the set of tracers to Ho, Sr, and W (Table 4-7). These same criteria of low p value, small hydrated radius, low ionic potential, and low electron affinity were again used. None co-occur together chemically and when graphed by sample site, they do not covary.

Table 4-7: Tracers that differentiate the Banks, Upland and Street Residue

Tracer (mg kg <sup>-1</sup> g <sup>-1</sup> )	Kruskal-Wallis	Bank Mean (N=18)	Bank CV	Streets Mean (N=2)	Street CV	Upland Mean (N=14)	Upland CV	Periodic Group
Ho (mg kg <sup>-1</sup> )	0.005	2.17	34.46	1.31	1.63	1.62	24.66	Lanthanide
Sr (mg kg <sup>-1</sup> )	0.043	58.23	19.37	117.75	22.04	57.12	17.63	Alkali Earth Metal
W (mg kg <sup>-1</sup> )	0.033	1.97	20.27	1.15	6.15	1.75	20.39	Transition Metal

Table 4-8: Estimation of Relative Sediment Source Contributions by Landscape Position using Tracers: Holmium, Strontium, and Tungsten

Date of Suspended Sediment Collection	Banks % Contributing	Banks flux (g/s)	Streets % Contributing	Streets Flux (g/s)	Upland % Contributing	Upland Flux (g/s)	Error
10/7/2005	98%	124.82	2%	2.55	0%	0.00	0.904
10/22/2005	85%	37.97	15%	6.70	0%	0.00	0.515
12/25/2005	11%	1.16	14%	1.47	75%	7.89	0.253
1/18/2006	12%	18.02	12%	18.02	76%	114.11	0.138
2/4/2006	90%	23.03	10%	2.56	0%	0.00	0.356
4/23/2006	85%	247.04	15%	43.59	0%	0.00	0.394
5/11/2006	82%	5.11	18%	1.12	0%	0.00	0.748
6/25/2006	0%	0.00	15%	4742.01	85%	26871.36	0.089
average	58%	2335.43	13%	508.23	30%	1189.90	0.424
fall average	92%	78.71	9%	7.31	0%	0.00	0.707
winter average	38%	23.41	12%	7.45	50%	31.23	0.249
spring average	56%	5924.67	16%	1701.88	28%	3010.20	0.41

The mixing model was applied to this source grouping (Table 4-8). The banks were the dominant contributing source in the fall and spring. The upland contributed more fine sediment to the stream in the winter and during the June 26 storm event. This event was the largest storm of the year and was a 200-year storm. The seasonal variation for the bank and upland samples indicates that leaf cover protects the upland areas from eroding fine sediment in the fall and spring. Leaf cover affects raindrop erosion. These data indicate different erosion mechanisms are in effect in different seasons of the year. More sloughing and mass wasting occurs in winter while overland erosion predominates in the summer.

The street residue contribution was consistently around 12%. It was not affected by seasonal variation. Its coverage, infiltration, and imperviousness are static. The one exception was the October 7, 2006 storm event. This event was a 30-year storm of 25 hours, 18 cm accumulated rainfall. The lower relative contribution reflects limited fine sediment supply and dilution. Our finding for street residue contribution is consistent with other researchers who found that roads may contribute 10-20% of sediment during smaller, low intensity storms (Burton and Pitt, 2002).

Any source with a limited availability of fine sediment will reach a maximum contribution. Once that maximum contribution has been reached, calculating relative contributions of fine sediment will necessarily make it appear that any source already at its maximum in terms of available sediment is contributing less on a proportional basis. This is a dilution effect.

#### ***Alternative Tracer Selection: Subwatershed***

To test the sensitivity of the criteria used to select the tracers and the mixing model, alternative tracers were selected from among those that were significantly different between the source groups. Using the same criteria of low p, one tracer per periodic group, small hydrated radius, lowest electron affinity, and the lowest ionic potential among those in that periodic group, we ran the mixing model with Ba, Bi, Sm and Th (Table 4-9).

Table 4-9: Alternative Tracers that Differentiate Sediment Sources by Hydrological Subwatershed Boundary

Tracer	Kruskal-Wallis	West Mean (N=10)	West CV (N=10)	East mean (N=15)	East CV (N=15)	Periodic Group
<b>Ba (mg kg<sup>-1</sup>)</b>	0.0001	508.88	31.39	310.69	21.93	Alkali Earth Metal
<b>Bi (mg kg<sup>-1</sup>)</b>	0.0002	0.36	47.29	0.18	35.24	Metal
<b>Sm (mg kg<sup>-1</sup>)</b>	0.0001	13.01	38.44	7.67	20.13	Lanthanide
<b>Th (mg kg<sup>-1</sup>)</b>	0.0004	16.18	23.87	11.43	18.57	Actinide

Selecting two different types of storms based on the hydrograph (Appendix E), these alternative tracers show different results when used in the mixing model (Table 4-10). These sources attributed to the suspended sediment vary significantly when a different set of tracers is used. Yet, both sets of tracers result in lower error than when

all of the possible tracers are used. The error is <1.0 with few tracers as opposed to errors <5.0 with all possible tracers. Fewer tracers produce better results, but the criteria for selecting those tracers and the behavior of the tracers in the erosion and transport process requires more investigation.

Table 4-10: Alternative estimation of Relative Sediment Source Contributions by Hydrological Subwatershed using tracers Barium, Bismuth, Samarium, and Thorium.

Suspended Sediment	West	West Flux	East	East Flux	Error
Date	% Contributing	(g/s)	% Contributing	(g/s)	
10/7/2005	31%	39.48	69%	87.88	0.886
1/18/2006	26%	39.04	74%	18.93	0.670

***Alternative Tracer Selection: Landscape Position***

To determine the sensitivity of the model to the selection of tracers, I used the same criteria of low p value, lowest ionic potential, largest atomic radius, and lowest electron affinity within the tracers still available from that periodic group. As an alternative, CaO, Cr<sub>2</sub>O<sub>3</sub>, and Gd were selected for analysis (Table 4-11).

Table 4-11: Alternative tracers that differentiate the Banks, Upland and Street Residue

Tracer (mg kg <sup>-1</sup> g <sup>-1</sup> )	Kruskal-Wallis	Bank Mean (N=18)	Bank CV	Streets Mean (N=2)	Street CV	Upland Mean (N=14)	Upland CV	Periodic Group
CaO (wt. %)	0.046	0.34	67.83	4.42	21.30	0.67	141.87	Alkali Earth Metal
Cr <sub>2</sub> O <sub>3</sub> (wt. %)	0.043	0.02	99.78	0.02	10.35	0.01	32.75	Transition Metal
Gd (mg kg <sup>-1</sup> )	0.018	10.18	43.42	5.96	3.68	7.38	40.60	Lanthanide

Table 4-12: Alternative Estimation of Relative Sediment Source Contributions by Landscape Position using Tracers: Calcium, Chromium, and Gadolinium

Date of Suspended Sediment Collection	Banks % Contributing	Banks flux (g/s)	Streets % Contributing	Streets Flux (g/s)	Upland % Contributing	Upland Flux (g/s)	Error
10/7/2005	65%	82.79	11%	14.01	24%	30.57	0.178
1/18/2006	90%	135.13	10%	15.01	0%	0.00	0.237

Using these alternative tracers overall reduced error to <1.0 when compared to using all possible tracers where error <4.0. However, using Ca, Cr, and Gd produced different results than when Ho, Sr, and W were used. Further investigation into the behavior of the tracers is required.

## Discussion

Testing the sediment fingerprinting approach in this urban watershed provided substantial challenges. Tracers of geogenic origin provide more significant differences among sources than tracers of anthropogenic origin. The process by which these tracers were chosen required an iterative approach of measuring the concentrations of 63 different elements. Only when beginning with so many tracers, and measuring the concentrations in both the sources and suspended sediment, could those appropriate for this watershed be selected. For future sediment fingerprinting research in urban areas, it is recommended to use geogenic tracers appropriate to the mineralogy and geology of the region.

There may be statistically equivalent solutions to the mixing model when using a large number of tracers. The solution to this problem is to eliminate the covarying tracers so there is only one solution to the mixing possible that produces the lowest error. The data show that fewer tracers among those that show significant differences in the sediment source groups are clearly more powerful. In selecting tracers, multicollinearity is a factor that must be considered. Where several tracers covary, only one may be selected. Otherwise, source groups that are overrepresented by specific tracers will be overrepresented in the results of the mixing model. The criteria for selecting specific tracers is critical to ensuring accurate results from the mixing model. The behavior of the tracers in the erosion and transport process must be conservative.

Finally, a careful interpretation of the attribution of the quantity of sediment from the sources must account for a dilution effect. The limited supply of sediment from some sources may weight a proportional contribution. This was seen in this data in that the street residue was consistently about 12% except where the rainfall volume was highest.

Overall, this method is viable for urban watersheds. The adaptations outlined in Chapter 3 and careful statistical analysis allow the sediment fingerprinting method to be effectively deployed to quantify sediment sources in the predominantly urban Northeast Branch Watershed.

## Chapter 5: Conclusions and Future Research

### Summary

This research identifies sediment sources of the suspended fraction in the Northeast Branch of the Anacostia River. After reviewing the existing literature on sediment source identification, and gathering some preliminary data from the watershed, the following three hypotheses were formed:

1. Chemical analyses of sediment can be used to determine the contributions of sediment sources in urban watersheds.
2. Sediment source compositions used in the sediment fingerprinting of urban watersheds will include anthropogenically enriched elements.
3. The primary source of suspended sediment in the Northeast Branch is derived from stream bank erosion.

To test these hypotheses in the Northeast Branch watershed, I conducted a soil survey to understand historical alluvial deposition patterns under land use change (forested, agricultural, urbanization). I mapped soil morphological variation (buried A horizons, texture, carbon, clay illuviation, and redoximorphic features) (Appendix A). Sites were informed by the use of GIS analysis using: stream maps (both NRCS and USGS), hydrological watershed boundary (USGS and NRCS), geology maps (Maryland Geological Society), land use (NLCD), topography (Digital Raster Graphic, USDA and NRCS), and the Soil Survey (Soil Survey Staff, 1967). In addition, I used Cs-137 and Pb concentrations to determine historical alluvial deposition patterns under land use change (Chapter 2).

I collected samples from potential sources of sediment at more than 25 sites in the watershed including from streambanks, point bars, flood plains, upland areas, and street residue (Appendix B) and suspended sediment samples from the Northeast Branch at the outlet of the watershed during eight storm events over the course of 12 months (Appendix E). These samples were analyzed for elemental and radionuclide concentrations (Appendix C). Additional data used in the analysis includes mean composition of the Earth's upper continental crust (Rudnick and Gao, 2003). Overall, I found tremendous variation in land use over space and time. The soils and geology also had significant differences, but were spatially more continuous. Therefore, these more continuous differences in soils and geology allow discrimination among sediment sources.

In order to evaluate whether elements commonly contributed from anthropogenic sources could be used to identify urban contributions to total suspended sediment, I used an enrichment ratio method to quantify anthropogenically enhanced elemental concentrations in watershed sediment. This allowed elements that are not a result of land use changes or point source contamination to be identified (Chapter 3). These



elements were also evaluated to determine whether they formed a distinct end-member that perhaps defined an urban signature in the watershed.

A multivariate mixing model related the sum of contributions from all the different sediment sources to the suspended sediment. In using this model, the goal is to minimize error while creating a vector of sources equal to 100%. The error term is standard deviation; therefore the tracers are normalized in the mixing model. To avoid issues of multi-collinearity, I selected those tracers that were most significantly different. Among those, I also selected tracers within each periodic group represented that had the smallest hydrated radius and lowest electron affinity (Chapter 4).

In terms of the hypotheses, my findings are as follows. First, there is support for using chemical analyses of sediment to determine sources in urban watersheds. The chemical tracers effectively discriminated among the sediment source groups. Second, sediment source compositions primarily were composed of geogenic elements, but the suspended sediment was primarily characterized by anthropogenic elements. Moreover, the suspended sediment concentrations were not bracketed by the sources, indicating a previously unidentified source group. This result did not support the second hypothesis. Further analysis showed that street residue closely approached the concentrations in the suspended sediment. Street residue is the only source that does not significantly dilute atmospheric particulate matter. This indicates that atmospheric particulate matter is one of the sources of the suspended sediment. This method allowed for identification of a missing source of sediment—atmospheric particulate matter. It also showed street residue as the most contaminated source of sediment (e.g., Hg, Pb, and Cd).

Third, on a mass basis, stream bank erosion was the primary source of suspended sediment in the Northeast Branch. As just noted, the primary constituents of the sediment were geogenic, but the contaminated sediment was related to street residue. Solving the mixing model provided the relative quantity of sediment generated by each source in the watershed. The eastern portion of the subwatershed contributed the most sediment to the fine sediment fraction. This is likely caused by the difference in the length of the travel path to station where the suspended sediment was collected. The banks contributed the most sediment during the fall and spring while the upland areas contributed the most in the winter. Thus, seasonal differences were significant—even in this urban watershed. The street residue contribution was consistently around 12% regardless of seasonal variation. Sediment storage on streets has a maximum capacity. A dilution effect on the percent contributed from the streets was evident for those storm events that generated more stream discharge.

This research also examined the use of radionuclides as sediment tracers. My results show that Cs-137 is not suitable for suspended sediment identification in this watershed. This is because of the rate of land use changes in the watershed. Cs-137 revealed patterns of erosion and storage moving downstream (Chapter 2). In the headwaters there was evidence of erosion while the mid-reaches of the streams showed erosion and sediment storage. The downstream reaches of the streams

showed erosion but little storage. This means that the sediment being eroded from the headwaters is not the same that passes through the gauge station on the Northeast Branch. Rather, it is sediment eroded from the mid-reaches that continues downstream because of a lack of sediment storage.

#### *Connections to Other Research*

Very few other studies have examined sources of suspended sediment in a dominantly urban watershed. One related study (Carter et al., 2003), examined sewage treatment waste solids and “road dust” as sources of sediment in the Rivers Aire and Calder watershed in central England. This watershed has stable land use patterns, well-identified land uses (cultivated, uncultivated and woodland), and good water quality upstream. The study area is not comparable to common urban/suburban watersheds in much of the United States. My research shows that the methods are applicable to a more common watershed environment in the Northeast of the United States. To successfully apply those methods, I used spatially defined source groups rather than land use.

#### *Future Research*

Future research could compare the current trace element concentrations to historic Chesapeake Bay sediment depth profiles (pre-1770) to illustrate anthropogenic differences specifically for this region rather than using the mean composition of the Earth’s upper continental crust. Differences in the methods used to measure trace elements will have to be controlled.

Historic deposition of tracers could also be addressed by partitioning the source samples into various depths and tracking historical movement of sediment. Other analyses could track the movement of metals more clearly by partitioning the organic matter into a separate fraction for analysis. Bonding to organic material by metals varies significantly depending on the speciation of the metals and other elements present. Additional research should tease apart how much of these tracers are bound to organics or sediment.

There may also be differences in sorption of the tracers to sediment associated with the fluctuating pH in this natural environment. However, the tracers used for the sediment mixing model were not ones that show a strong dependence upon pH within the range of pH values found in natural and urban stream channels. In this analysis, I dissolved the sediment rather than using multiple leachates; the enrichment ratio analysis suggests that meal contamination was overprinted onto much of the sediment. Partial dissolution of the sediment could be conducted to determine this.

Because atmospheric deposition appeared to be an end-member composition, further analyses should measure the composition of atmospheric particulate matter deposited in the watershed and the composition of sewage. The components of fertilizers used on urban lawns and on the farms at Beltsville Agricultural Research Center should

also be determined. By examining what tracers co-vary with K, K-40, and P<sub>2</sub>O<sub>5</sub>, it can be determined how much of these tracers are anthropogenic.

Finally and most importantly, researchers should address travel times by sampling over the course of the hydrograph using a flow-integrated sampler (Phillips et al., 2000). Such as sampler, placed into the stream at the beginning of a storm event, and would collect sediment over the entire storm event.

### Conclusion

This research began with a concern for sediment as a pollutant in the Chesapeake Bay. On a mass basis most sediment is originating from stream banks. However, I found that the most contaminated sediment (e.g., Pb, Hg, and Cd) was coming from atmospheric particulate matter deposited onto roadways, parking lots and other impervious surfaces, which are then washed into streams.

Land in urban watersheds in the Northeast United States increasingly is covered with roadways, parking lots, and other impervious surfaces. Any policy that seeks to mitigate water-born pollution from such lands must recognize the need for soils to dilute atmospherically deposited material rather than allow it to wash into rivers and streams.

Overall, the sediment fingerprinting method is useful in an urban watershed with modifications. Since the physical, chemical, and biological processes in soils and streams are integrated by our watersheds, these systems continue to be worth studying to discover the sources of sediment as well as the sources of the most contaminated sediment.

## Appendix A: Soil Descriptions

### ***Paint Branch***

Site P1 (Fairland):

Date of description: 3/3/06

Slope: complex concave

Vegetation/Land Cover: Intermixed hardwood and shrub near stream. Ball fields on summit.

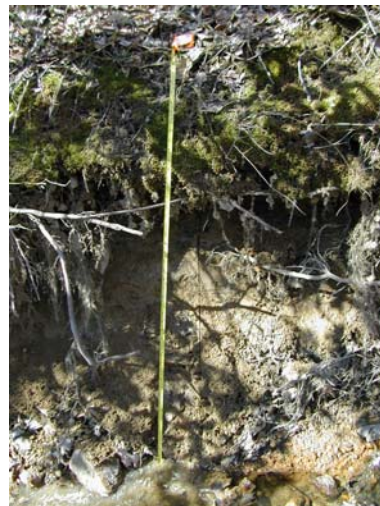
Bank Height: 87 cm, of which 3 cm was submerged by the stream

Site P1. Undercutting of bank and hanging roots gave evidence of active erosion. The channel was narrow (~3 feet).

Horizon	Depth (cm)	Texture	Mineralogy	Concentrations/Depletions: Quantity and Contrast	Roots	Comments
B/A	87	Sandy Loam	micaceous	Concentrations: Iron masses along old root channels, common, distinct. Depletions: prominent common	Few	Unconsolidated material. 2% rock frags, few, large.



Site P1 stream and bank



Site P2 (Powder Mill Road):

Date of description: 3/3/06

Slope: simple, linear. Very steep incline to terrace or summit position

Vegetation/Land Cover: Intermixed hardwoods and conifers

Bank height: 200 cm, of which 16 cm is submerged by the stream.

Site P2. The stream channel was greater than 6 meters and was a gravel/boulder bottom.

Horizon	Depth in cm	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast:	Roots	Comments
B/A	200	loam	Less mica than upstream, but still present	none	Many roots	20% cobbles 10 cm or larger in diameter



Site P2 stream and bank

Site P3, P4, Pdump:

Currently under construction; access to bank is limited. Past observation indicates that the high bank material is similar to Site I3 with a layer of ironstone causing a perched water table.



Site P3 and P4 (both banks) of stream during 3/06 renovation

### ***Little Paint Branch***

Site L1 (near residential area on golf courses, <10 years old):

Date of description: 3/3/06

Slope: simple concave  
 Vegetation/Land Cover: swamp-trees, shrubs  
 Bank Height: 162 cm, of which 5 cm was submerged by the stream.

Site L1. Undercutting of bank and hanging roots gave evidence of active erosion.  
 Gravel bottom stream with moderate channel width (~4 meters).

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast	Roots
A	142	Gradual	Silt loam	Micaceous	None	common
Bw	157		Silt loam but increasing sands	Mixed		common



Site L1 stream and bank



Site L2 (Cherry Hill Road):  
 Date of description: 3/3/06  
 Slope: simple, linear  
 Vegetation/Land Cover: Intermixed hardwoods and conifers  
 Bank height: 184 cm, of which 10 cm is submerged by the stream. Bank slopes slightly back to the floodplain



Site L2. Hanging roots gives evidence of active erosion. At other locations along this reach of the stream there is an Ab horizon.

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity And Contrast	Roots	Comment
C1	15	Abrupt	Sandy loam (clay=16%)	mixed	None	few	
C2	40	Abrupt		mixed			cobble line
2Bt	105	Abrupt	Silty clay loam	mixed	Common, distinct iron concentrations		



Site L2 stream and bank. Note cobble line in bank  $\frac{1}{4}$  from top of ground

### ***Indian Creek***

Site I3 (still a farm):

Date of description: 3/3/06

Slope: complex concave.

Vegetation/Land Cover Intermixed hardwoods and conifers along stream edge. Crop uplands.

Bank height: 180 cm, of which 9 cm is submerged by the stream.

Site I3. This site shows the Arundel Clay from the Cretaceous Period.

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast	Roots	Comments
A	40	Abrupt	Loamy coarse sand	mixed	None	many	
C1	85	Abrupt	Loamy coarse sand	mixed			
C2	135	Abrupt	Silty clay loam	mixed			yellow-brown/white striated or banded
C3	185		Silty clay loam	mixed			reddish



a)



b)



c)



d)

Site I3 stream (a) and bank (b), close up of shadowed upper bank (c), and close up of lower bank (d).

Site I2 (Black Angus farm):

Date of description: 3/3/06

Slope: simple concave.

Vegetation/Land Cover: Intermixed hardwoods and conifers near stream, crop on terrace.

Bank height: 125 cm, of which 1 cm is submerged by the stream.



Site I2. Cows have access to the stream and cut into the banks. In addition, the October 8, 2005 storm incised the bank approximately 0.5 meter.

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast	Roots
A	60	Gradual	Silt loam (clay=7%)	mixed	None	
Bt	124		Silt loam (Clay=15%)	mixed		



Site I2 stream and bank

Site I4 (industrial area):

Date of description: 3/3/06

Slope: buildings and parking lots on what may have once been a floodplain.

Vegetation/Land Cover: Urban—cement with lots of garbage

Bank height: 120 cm, of which 1 cm is submerged by the stream. Bank slopes away from stream.

Site I4. The stream has a gravel bottom with bars and the channel is approximately 4 meters. I noted that there are tags tied to the few shrubs that say “wetlands”.

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast:	Roots	Comments
Bw	120		loamy sand	mixed	None	None	All very recent fluvial deposit. Terraced



Site I4 stream and bank

Site I5 (Berwyn Heights):

Date of description: 3/4/06

Slope: simple and concave.

Vegetation/Land Cover; Stream banks are shrubs with some hardwoods. Terrace is a playground. Upslope are houses.

Bank height: 100 cm of which 12 cm is submerged by the stream.

Site I5. On opposite side of stream there are some gravel deposits. The stream is approximately 20 feet wide and the bottom is gravelly.

Horizon	Depth in cm	Boundary Abrupt, clear, gradual	Texture	Mineralogy	Concentrations Quantity Contrast:	Roots
Bw	88		Silt loam (clay=8%)	Some mica present	None	Few



a)



b)



c)

Site I5 stream (a), close-up of opposite bank (b), and bank described above (c). Note that the tire was deposited in the bank, and is now being eroded and exposed.

### ***Beaverdam Creek***

Site B1 (OPEIII):

Date of description: 3/4/06

Slope: simple concave

Vegetation/Land Cover: swamp-trees, shrubs and corn upslope

Bank height: 30 cm, of which 5 cm is submerged by the stream. In some places, the bank height is less than 5 cm.

Site B1

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast:	Roots
Bt	10	Clear	Clay loam	siliceous	Concentrations: Few, distinct iron masses. No depletions	few
Btg	25		Clay loam	siliceous	Concentrations: Few, distinct iron masses. Depletions: Matrix color is gleyed	



Site B1 floodplain auger boring. No available picture of bank described above.

Site B3 (Plant Materials Center):

Date of description: 3/4/06

Slope: complex concave

Vegetation/Land Cover: swamp-trees, shrubs and hay upslope

Bank height: 150 cm, of which 56 cm is submerged by the stream.

Site B3. In many places, there is an exposed buried A. There are bars and the stream bottom is sand. Many fallen logs criss-cross the stream. Active incision evident.

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast:	Roots
A	25	Clear	Silt loam (Clay=7%)	mixed		common
Bt	40	Clear	Loam (Clay=15%)	mixed	Many distinct iron spherical concentrations. No depletions	
Ab	60	Gradual	Loam (Clay=22%)	mixed	Many distinct iron spherical concentrations. No depletions	
Bw	94	Gradual	Sandy loam	Siliceous		



Site B3 stream. Note buried A horizon.

Site B4 (marsh on Research Road)

Date of description: 3/6/06

Slope: simple linear

Vegetation/Land Cover: Shrubs. There are some hardwoods upslope.

Bank height: 54 cm, of which 14 cm is submerged by the stream.

Site B4

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast	Roots
Bw/C	40		Sandy clay loam (clay=24%)	mixed	Common distinct spherical iron concentrations. Gleyed matrix at water's edge	many



Site B4 stream and close-up of redoximorphic features in the bank

Site B2 (Mandan Road at BW Pkwy):

Date of description: 3/4/06

Slope: Densely residential and very close to road. Unable to determine slope.

Vegetation/Land Cover: swamp-trees, shrubs

Bank height: 35 cm, of which 3 cm is submerged by the stream.

Site B2. Silty bottom stream that is about 0.5 meter across at a maximum.

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast:	Roots
C	1	Abrupt	Sand	siliceous	none	
Bw	27	Clear	Silt loam (15% clay)	mixed		
Bt	30	Clear	Clay loam (30% clay)	mixed		





Site B2 stream

***Northeast Branch of the Anacostia River***

Site PM5 (just below confluence of Indian and Beaverdam Creeks):

Date of description: 3/6/06

Slope: simple linear

Vegetation/Land Cover; Stream banks are intermixed hardwoods and conifers.  
Upslope is urbanized.

Bank height: 150 cm, of which 10 cm is submerged by the stream.

Site PM5

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast	Roots	Comments
C	140	clear	Sandy loam	mixed	none	many	1 cm diameter mica flakes
Ab?	150	Possible buried A at waters edge. Unable to determine source of organic material in the horizon because it was under water.					



Site PM5 stream.

Site PM6 (near 94<sup>th</sup> Aero squadron):

Date of description: 3/6/06

Slope: simple concave.

Vegetation/Land Cover; Stream banks are shrubs with some hardwoods. Upslope is urban.

Bank height: 156 cm, of which 95cm is submerged by the stream.

Site PM6. Just above this is a berm to slow velocity. Stream has a gravel bottom interspersed with large granite rocks that the stream has moved. The rocks evidently came from an attempt at armoring the banks. There are hanging roots that indicate active erosion of the channel.

Horizon	Depth in cm	Boundary Abrupt, clear, gradual	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast	Roots Few common	Comments
C	2	Abrupt	Sandy	Lots of mica and sand.	none		
A/B	59		Sandy loam (clay=13%)	mixed		many	

Site PM7 (near gauge):

Date of description: 3/6/06

Landscape: there is a floodplain approximately 2.5 meters wide. The terrace is a park and playground.

Vegetation/Land Cover: Urban.

Bank height: 110 cm of which 5 cm is submerged by the stream.

Site PM7, gauge site. Heavy plastering of sediment, branches up to an inch in diameter, leaves oriented vertically on bank, and garbage such as plastic bags. Gravel bottom bed with lots of algae. Algal growth probably supported by sewage overflows. Just above this is a berm to slow velocity.

Horizon	Depth in cm	Boundary	Texture	Mineralogy	Concentrations/ Depletions: Quantity and Contrast:	Roots
C	105		Loamy sand	siliceous	none	common



Site PM7 stream and bank



## Appendix B: Distribution of Sediment Source Samples

Source Type	Landscape Position	Land Use	No. of Samples
Coastal Plain Physiographic Region	Upland	Urban	1
		Rural	1
		Forested	1
	Floodplain	Urban	0
		Rural	1
		Forested	1
	Bank	Urban	11
		Rural	3
		Forested	2
	Point Bar	Urban	3
		Rural	0
		Forested	1
Piedmont Physiographic Region	Upland	Urban	1
		Rural	0
		Forested	1
	Floodplain	Urban	0
		Rural	0
		Forested	1
	Bank	Urban	3
		Rural	0
		Forested	1
	Point Bar	Urban	0
		Rural	0
		Forested	0
Storm Events (same sample site, sampled over time)			8
Construction site			1
Street Residue (6 sites aggregated, sampled over time)			2
Total			43

## Appendix C: Raw Data

Site	Subwatershed	Region	pos	stream	Cum. Distance Downstream from headwaters	Calculate d. Unsieved Cs-137	SIEVED Cs-137	K-40	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	
					m	Bq/kg	Bq/kg	Bq/kg	%	%	%	%	%	%	%	%	%	%	
A	West	Coastal_Plain	PB	P				0.000	3426.260	68.62	11.60	5.90	0.77	0.52	0.63	1.93	1.90	0.16	0.15
P4	West	Coastal_Plain	B	P	18110			0.00	628.79	70.26	13.17	4.65	0.67	0.27	0.59	2.22	1.54	0.11	0.11
Pdump	West	Coastal_Plain	B	P	18108	0.93		9.51	340.31	63.09	11.82	7.52	0.51	0.61	0.31	1.54	1.02	0.25	0.22
P3	West	Coastal_Plain	B	P	18109			0	791.34	68.08	16.64	1.46	0.29	0.10	0.06	1.12	2.35	0.07	0.01
PM6	Mixed	Coastal_Plain	B	N	172	0.36		1.99	460.50	71.77	10.39	4.89	0.70	0.40	0.37	1.42	1.83	0.12	0.11
P2	West	Piedmont	B	P	13368	0.00		0.00	928.09	66.32	13.36	5.46	0.78	0.55	0.52	2.18	1.83	0.12	0.11
C	West	Piedmont	FP	P	13368			39.476	732.449	59.90	15.89	6.14	0.83	0.22	0.49	2.28	1.50	0.13	0.11
C	West	Piedmont	U	P	13368			29.714	801.144	51.94	16.39	6.97	1.19	0.35	0.63	2.69	1.23	0.18	0.22
PM7	Mixed	Coastal_Plain	B	N	2458	0.00		0.00	863.06	68.44	10.27	5.61	0.73	0.45	0.30	1.33	1.40	0.16	0.23
D_EW	Mixed	Coastal_Plain	PB	N				0.000	1366.380	78.61	6.63	3.56	0.29	0.27	0.23	0.86	1.16	0.14	0.07
D_RIVER RD	Mixed	Coastal_Plain	PB	N				0.000	1094.670	73.22	9.14	5.44	0.65	0.47	0.31	1.32	1.81	0.15	0.11
I5	East	Coastal_Plain	B	I	10612	0.82		4.53	440.59	69.47	10.54	5.11	0.86	0.56	0.23	1.18	1.10	0.15	0.20
Earth	Crustal	Earth	Earth	Earth	0				66.60	15.40	5.04	2.48	3.59	3.27	2.80	0.64	1.15	0.10	0.10
L1	West	Piedmont	B	L	5727	4.77		13.88	826.95	64.13	13.97	5.17	0.84	0.37	0.44	1.93	1.58	0.16	0.09
L2	West	Coastal_Plain	B	L	12358	0.00		0.00	885.46	10.44	4.78	0.80	0.63	0.50	1.45	1.80	0.15	0.14	
B4	East	Coastal_Plain	B	B	5688	3.29		8.65	392.35	76.49	6.96	3.48	0.38	0.20	0.26	1.21	1.12	0.12	0.06
B1	East	Coastal_Plain	B	B	3183	2.13		12.12	663.76	61.06	11.25	5.01	0.36	0.27	0.19	1.26	0.91	0.26	0.03
I	East	Coastal_Plain	U	B	3183			25.456	1086.636	75.60	6.55	3.03	0.51	0.47	0.45	1.88	1.19	0.19	0.05
I	East	Coastal_Plain	FP	B				34.05	2342.38	56.27	12.98	4.88	0.41	0.26	0.16	1.41	0.92	0.29	0.03
I_a	East	Coastal_Plain	B	B				16.95	2068.57	61.48	11.31	4.52	0.34	0.16	0.18	1.26	0.92	0.21	0.03
I_b	East	Coastal_Plain	B	B				17.49	1473.24	62.31	12	3.32	0.36	0.15	0.19	1.32	0.94	0.22	0.02
I_c	East	Coastal_Plain	B	B				12.58	1151.88	62.51	11.46	4.49	0.35	0.16	0.17	1.25	0.97	0.23	0.02
PM5	Mixed	Coastal_Plain	B	N	0	0.45		4.28	635.40	67.44	12.62	5.48	0.95	0.50	0.46	1.70	1.59	0.13	0.13
I4	East	Coastal_Plain	B	I	5151	0.16		3.52	4.16	69.14	6.70	4.17	1.02	0.93	0.30	1.16	1.15	0.15	0.16
I3	East	Coastal_Plain	B	I	1657	0.00		0.00	4.26	66.15	19.33	3.54	0.20	0.03	0.14	1.20	1.26	0.07	0.01
MSQUARE	Mixed	Coastal_Plain	U	N	70			0.000	1232.263	48.91	22.89	9.18	2.54	1.24	0.49	2.57	0.85	0.14	0.14
I2	East	Coastal_Plain	B	I	1656	0.00		0.00	490.90	76.33	9.34	2.93	0.39	0.21	0.42	1.55	1.23	0.10	0.07
B2	East	Coastal_Plain	B	B	501	0.00		0.000	717.209	76.73	9.77	3.61	0.48	0.21	0.38	1.49	1.13	0.08	0.03
O	East	Coastal_Plain	FP	B	501			5.269	416.360	77.37	6.45	3.24	0.55	0.70	0.23	0.90	1.07	0.11	0.05
O	East	Coastal_Plain	U	B	501			37.656	909.650	68.08	9.80	2.64	0.32	0.16	0.24	1.22	1.00	0.10	0.01
P1	West	Piedmont	B	P	6467	0.00		0.000	886.320	63.68	16.68	4.00	0.65	0.13	0.48	3.15	1.43	0.12	0.03
P	West	Piedmont	U	P	6467			9.209	1380.977	62.62	15.66	5.70	0.69	0.18	0.37	2.39	1.45	0.14	0.08
P_a	West	Piedmont	B	P				0	1243.23	63.31	16.14	4.19	0.65	0.15	0.51	2.92	1.4	0.13	0.03
P_b	West	Piedmont	B	P				7.24	1034.39	69.43	14.24	3.12	0.74	0.31	0.77	2.39	1.42	0.07	0.03
P_c	West	Piedmont	B	P				4.16	679.47	71.35	12.54	3.79	0.55	0.2	0.67	2.27	1.25	0.07	0.03
B3	East	Coastal_Plain	B	B	5188	0.31		2.476	504.611	78.20	6.44	3.70	0.31	0.11	0.25	1.11	1.23	0.09	0.05
Q	East	Coastal_Plain	FP	B	5188			14.270	573.053	70.18	10.58	3.76	0.49	0.19	0.33	1.48	1.10	0.15	0.09
Q	East	Coastal_Plain	PB	B				3.44	943.34	74.93	7.75	5.7	0.65	0.49	0.32	1.23	2.39	0.13	0.11
Q	East	Coastal_Plain	U	B	5188			61.109	960.451	72.98	8.23	3.82	0.20	0.08	0.14	0.80	0.98	0.12	0.01
I1	East	Coastal_Plain	B	I				8.3	532.03	78.38	8.81	2.22	0.44	0.2	0.5	1.52	1.28	0.09	0.05
PU1	West	Piedmont	U	P				0	1700.82	41.32	22.19	8.55	0.77	0.58	0.21	2.46	1.24	0.26	0.12
SE 10-22-05	Mixed	Coastal_Plain	SE	N	2458			0.000	1757.416	62.96	14.52	5.77	1.09	0.63	0.32	1.73	1.15	0.23	0.28
SE 10-7-05	Mixed	Coastal_Plain	SE	N	2458			4.360	2660.290	63.22	10.88	6.36	1.07	0.66	0.30	1.46	1.01	0.32	0.28
SE 1-18-06	Mixed	Coastal_Plain	SE	N				6.09	1375.58	61.7	13.51	5.77	1.02	0.74	0.27	1.47	1.16	0.21	0.16
SE 12-25-05	Mixed	Coastal_Plain	SE	N				0	1336.95	63.63	12.12	5.62	1.03	0.84	0.37	1.45	1.14	0.21	0.1
SE 3-9-06	Mixed	Coastal_Plain	SE	N				3.89	118.3	70.32	10.08	4.75	0.61	0.71	0.26	1.28	1.12	0.16	0.07
SE 4-23-06	Mixed	Coastal_Plain	SE	N				5.57	1713.33	63.66	14.14	5.07	0.77	0.5	0.38	1.8	1.09	0.19	0.22
SE 5-11-06	Mixed	Coastal_Plain	SE	N				3.36	779.14	59.09	10.79	6.08	1.47	1.65	0.31	1.4	0.95	0.3	0.16
SE 6-26-06	Mixed	Coastal_Plain	SE	N				5.090	781.400	64.14	12.19	5.64	0.98	0.74	0.28	1.44	1.03	0.26	0.1
Stop-n-school	Mixed	Coastal_Plain	U	N				0.000	1699.630	70.27	11.41	5.56	0.57	0.37	0.19	1.55	1.22	0.1	0.04
Street Residue Fall	Mixed		Streets					6.4	472.64	52.82	9.29	6.59	2.79	5.08	0.73	1.43	1.37	0.27	0.11
Street Residue Spring	Mixed		Streets					12.61	520.94	52.36	9.91	6.06	2.58	3.75	0.67	1.38	1.38	0.3	0.1
PU3	West	Piedmont	U	P				33.77	834.06	63.58	11.91	4	0.59	0.53	0.37	1.84	1.3	0.37	0.07
PU2	West	Piedmont	FP	P				43.77	737.86	63.47	13.32	4.1	0.5	0.16	0.38	2.19	1.17	0.11	0.04
BU1	East	Coastal_Plain	U	B				9.11	691.56	78.94	7.53	2.86	0.35	0.27	0.26	1.24	1.19	0.21	0.14
PMU2	Mixed	Coastal_Plain	U	N				13.91	694.79	74.01	7.96	2.99	0.37	0.38	0.33	1.36	1.16	0.22	0.1
IU1	East	Coastal_Plain	U	I				10.01	869.14	74.53	9.57	2.77	0.45	0.43	0.39	1.48	1.19	0.25	0.04
PMU1	Mixed	Coastal_Plain	U	N				19.91	659.4	67.4	8.18	3.25	0.61	0.38	0.33	1.37	1.08	0.29	0.06
IU2	East	Coastal_Plain	U	I				8.39	463.57	74.53	7.8	2.57	0.43	0.47	0.3	1.26	1.17	0.27	0.08

Site	Cr2O3	N	Sc	LOI	TOT_C	TOT_S	SUM	Ba	Be	Co	Cs	Ga	Hf	Nb	Rb	Sr	Ta	Th	U	V	
	%	mg/kg	mg/kg	%	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
A	0.012	54	13	7.1	1.34	0.06	99.77	415.5	3	25.5	2.9	15.6	33.6	27.7	77.1	8	65.1	2	13.6	6	107
P4	0.01	21.00	11.00	6.20	0.73	0.04	99.80	575.50	3.00	16.10	4.00	17.70	25.90	25.50	62.80	4.00	67.80	1.90	15.20	5.20	92.00
Fdump	0.01	40.00	10.00	12.70	3.39	0.05	99.61	603.70	2.00	13.4	3.4	16	13.5	18.3	70.7	365	69.4	1.4	11.1	4	90
P3	0.01	20.00	22.50	7.50	0.14	0.03	99.67	265.45	2.00	7.3	2.05	26.4	34.7	26.9	47.55	3	24.65	1.85	14.7	4.8	212.5
PM6	0.01	45.00	11.00	7.50	1.72	0.04	99.52	385.40	2.00	10.00	3.10	14.20	59.90	28.80	59.20	4.00	60.30	2.30	16.30	6.70	96.00
F2	0.01	43.00	11.00	8.40	1.62	0.03	99.65	540.40	2.00	15.10	3.90	17.80	32.40	29.70	88.10	4.00	73.20	2.40	15.60	6.10	95.00
C	0.01	43.00	13.00	12.40	3.17	0.05	99.91	511.90	3.00	17.6	4.3	20.3	26.5	25.6	100.6	5	68.2	2.3	16	5.4	106
C	0.01	45.00	13.00	16.10	4.45	0.11	99.91	760.10	6.00	20.1	5.9	22	17.3	23.2	138	4	78.3	2	14.1	4.3	102
PM7	0.02	75.00	11.00	10.60	2.72	0.05	99.55	369.60	2.00	45.20	3.30	13.50	50.10	22.40	55.70	4.00	55.50	1.70	14.40	6.00	94.00
D_EW	0.008	31	9	7.6	2.41	0.04	99.84	209.3	2	28.1	2.1	9.6	28.4	20.6	46	6	41.9	1.4	10.9	4.1	72
D_RIVER RD	0.019	44	13	7.1	1.67	0.06	99.75	265	2	28.1	2.2	12.1	36.3	26.2	60.1	4	52.7	1.7	14	5.1	103
I5	0.07	62.00	11.00	10.20	2.64	0.05	99.67	339.20	2.00	31.30	2.60	12.40	16.90	16.40	51.50	3.00	50.50	1.10	9.60	3.60	86.00
Earth		47	14.00					628	2.1	17.3	4.9	17.5	5.3	12	84	2.1	320	0.9	10.5	2.7	91
L1	0.01	46.00	11.00	11.10	2.55	0.04	99.80	451.40	3.00	15.00	4.10	17.70	28.40	24.90	61.50	3.00	59.30	2.10	17.70	6.00	92.00
L2	0.01	45.00	10.00	9.40	2.41	0.04	99.57	398.60	2.00	23.00	3.00	14.80	50.00	28.00	59.50	3.00	73.00	2.40	21.90	6.60	86.00
B4	0.01	32.00	9.00	7.50	1.88	0.03	99.78	327.00	2.00	22.80	3.30	12.80	17.40	20.50	63.70	3.00	53.30	1.50	9.70	3.90	76.00
B1	0.01	40.00	11.00	19.30	6.44	0.09	99.92	335.80	3.00	20.60	4.60	15.40	9.00	16.70	75.20	2.00	62.00	1.30	10.90	3.50	92.00
I	0.01	18.00	9.00	8.00	2.15	0.01	99.93	353.40	1.00	9.5	2.7	10.6	22.2	21.7	66.9	3	62.7	1.6	11	4.2	68
I	0.011	33	13	22.3	7.73	0.05	99.93	325	4	16.6	4.9	17.5	5.2	16.5	82.9	6	62.7	1.1	9.7	3.7	106
I_a	0.008	30	11	19.5	6.02	0.05	99.93	289.6	3	16.3	4.5	14.1	6.9	16.6	73.5	3	54.6	1.1	9.7	3.8	96
I_b	0.009	32	12	19.1	6.12	0.06	99.94	300.3	3	16	4.5	14.3	9	16.7	78.3	4	57.4	1.2	11.1	4	103
I_c	0.009	41	12	18.3	6.27	0.06	99.93	291	3	19	4.5	15.6	9.4	17.3	74.3	3	55.2	1.2	9.6	3.6	94
PM5	0.02	54.00	12.00	8.60	1.65	0.04	99.62	431.50	2.00	23.10	3.10	16.30	35.30	25.10	66.90	4.00	66.30	2.00	16.20	5.70	99.00
I4	0.05	50.00	10.00	12.40	3.18	0.06	99.32	502.80	1.00	18.40	2.50	10.20	30.50	17.10	51.30	5.00	61.80	1.50	13.40	4.20	75.00
I3	0.01	5.00	17.00	7.50	0.13	0.01	99.84	251.60	1.00	1.80	2.50	21.20	6.90	19.10	50.90	3.00	60.50	1.80	13.90	4.20	129.00
MSQUARE	0.02	73.00	37.00	11.00	0.49	0.01	99.98	628.90	3.00	25.2	6	27.2	11.5	16	116.7	3	72	1	22.4	4.4	183
I2	0.01	14.00	9.00	6.80	1.20	0.01	99.38	343.90	1.00	8.00	2.50	9.90	18.60	17.80	63.40	2.00	50.20	1.60	11.50	4.00	61.00
B2	0.01	19.00	10.00	6.00	0.78	0.04	99.93	321.10	1.00	7.5	2.8	12.2	22.6	20.1	63.6	2	55.5	1.6	14	4	81
O	0.01	24.00	9.00	9.20	3.13	0.02	99.89	216.10	1.00	13	1.8	8.1	23.8	18.1	37.4	2	48.5	1.5	11.1	3.8	61
O	0.01	15.00	9.00	16.20	6.03	0.12	99.98	269.20	1.00	4.9	2.9	13	13.7	17.9	57.9	3	53.6	1.4	9.5	3.2	81
P1	0.01	32.00	14.00	9.50	1.97	0.02	99.87	857.70	4.00	13.1	4.6	21.8	26.5	26.7	118.5	3	67.4	2	17.3	6	90
P	0.01	29.00	13.00	10.60	1.99	0.01	99.89	517.50	4.00	14.6	5.9	19.1	27	25.9	105.5	3	57.9	2.3	19.6	7.9	90
P_a	0.01	38	13	10.3	1.61	0.02	99.75	778.3	3	13.2	3.9	20.4	25.6	25.9	127.2	3	62	1.8	16.3	6.2	96
P_b	0.01	29	13	7.3	0.53	0.01	99.83	413.4	2	8.1	3.3	18.1	20.8	22.4	92.6	2	76.5	1.7	17.5	6	107
P_c	0.01	38	11	7.1	0.94	0.01	99.84	402.9	2	6.3	3.3	16.9	20	20.6	88.6	3	65.6	1.6	16.9	5.1	81
B3	0.01	28.00	10.00	6.40	1.36	0.04	99.91	276.80	3.00	18.2	2.8	11.1	23.5	22.2	56.7	2	47.1	1.6	13.9	4.2	76
O	0.01	31.00	10.00	11.60	3.71	0.02	99.94	377.80	2.00	19.2	3.6	13.5	16.1	20	75.4	3	57.1	1.5	11.1	3.6	73
O	0.017	45	13	5.9	1.35	0.07	99.83	244.9	2	23.6	1.8	9.5	55.6	29.7	49.2	6	48.1	2.2	17.1	6.5	85
O	0.01	11.00	9.00	12.60	4.61	0.05	99.97	184.70	1.00	3.3	1.9	11.4	15.4	16.8	42.1	3	40.3	1.4	9.6	2.7	70
I1	0.008	14	8	8.4	1.41	0.02	99.88	315.6	1	5.1	2.6	11.3	17.6	21.7	67.6	3	58.9	1.6	11.9	3.9	64
PU1	0.009	43	16	22.1	5.2	0.05	99.81	480.5	3	26.4	3.8	29.4	24.8	24.4	102.7	5	46.7	2.4	23.4	6	116
SE 10-22-05	0.02	74.00	15.00	11.20	3.08	0.08	99.92	430.50	2.00	51	4.1	18.5	10.3	20	77.9	5	66.8	1.5	11.2	3.2	105
SE 10-7-05	0.02	95.00	12.00	14.10	5.30	0.10	99.89	380.70	3.00	55.6	3.8	12.9	10.3	16.9	64.4	4	63	1.3	8.7	3.3	90
SE 1-18-06	0.017	60	15	13.6	4.02	0.07	99.87	329.6	2	42.9	3.7	18.3	9.9	17.9	78.2	5	64.3	1.2	10.6	3.5	119
SE 12-25-05	0.017	58	13	13.1	3.62	0.07	99.83	325.3	2	28.9	3.3	15.1	12.3	19.6	73.5	5	65.6	1.2	10.5	3.6	106
SE 2-9-05	0.012	47	12	10.3	3.25	0.05	99.87	288	2	27.3	3.3	13.7	14.2	19.3	67.9	4	65.7	1.5	10	3.5	93
SE 4-23-06	0.019	56	13	12	3.11	0.05	99.85	306.5	2	35.2	3.8	17.8	7.7	19.3	86.2	6	68.4	1.4	11.4	3.7	107
SE 5-11-06	0.015	79	12	17.6	6.73	0.13	99.85	260.4	3	53.1	3.2	15.8	10.4	16.1	70.5	5	69.1	1.2	8.6	3.4	102
SE 6-25-06	0.019	66	13	12.8	3.6	0.07	99.73	301.5	2	42.9	3.1	16.8	9.9	18.4	78	4	66.1	1.3	9.6	3.4	108
Slope near school	0.01	32	13	8.6	1.38	0.01	99.9	271.1	1	13.7	4.2	14.8	12.7	20.7	97.3	3	49.9	1.3	11.2	3.5	93
Street Residue Fall	0.022	69	13	19.3	8.78	0.19	99.81	297	1	20.5	2.2	13.2	20.2	18.6	61.6	7	136.1	1.4	9.7	3.9	155
Street Residue Spring	0.019	76	13	21.3	9.68	0.19	99.82	310.1	1	17.6	2.1	12.8	19	19.4	57.2	4	99.4	1.4	10.9	3.8	145
PU3	0.011	26	11	15.3	4.75	0.03	99.88	379.6	1	11.2	2.7	16	13.2	22.1	77.9	4	57.6	1.7	9.6	5	85
PU2	0.01	22	11	14.4	3.94	0.02	99.85	441.3	2	7	4.8	16.9	15.8	22.7	106.6	4	53.8	1.9	11.6	5	88
BU1	0.008	35	8	6.9	1.76	0.02	99.9	298.8	2	21.4	3.1	10.1	14.2	21.1	73.7	3	50	1.4	9.3	4	56
PMU2	0.008	22	8	11	3.48	0.03	99.89	320.1	1	10.1	2.2	10.3	14.5	19.1	72.1	6	53	1.3	9.1	3.8	56
U1	0.008	16	9	8.8	2.27	0.02	99.91	337.3	1	9.1	3.3	12.4	11.7	21	79.7	3	57.9	1.3	9.6	3.9	58
PMU1	0.009	19	8	13.3	4.03	0.03	99.88	276.9	1	8.6	2.3	10.4	14.1								

Site	W	Zr	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Mo	Cu	Pb	Zn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
A	1.5	1279	73.3	50.5	130.3	14.26	51.1	11	2.01	9.72	1.8	11.57	2.55	6.97	1.05	6.92	1.09	1.2	62.2	38.8	136
P4	1.80	824.20	71.20	58.40	155.60	17.16	65.00	13.10	2.72	12.31	2.12	12.36	2.51	7.58	1.28	7.43	1.15	0.70	23.40	17.30	50.00
Pdmp	3.1	473.6	38.3	42.5	96.3	9.95	37.5	7.2	1.33	5.04	1.09	6.44	1.36	3.66	0.65	4.14	0.66	1.4	158.8	773.2	2003
P3	3	1214.45	79.35	70.9	181.1	19.62	80.9	18.5	4.275	16.46	2.725	15.455	3.05	8.48	1.35	8.255	1.335	0.1	33.6	14.9	4
PM6	1.90	2,125.70	74.90	60.50	136.30	15.01	57.30	11.20	2.03	10.03	1.87	11.77	2.54	8.00	1.32	8.54	1.45	2.10	70.10	39.60	95.00
P2	1.90	1,107.10	70.20	60.30	144.10	14.72	55.70	11.50	2.12	10.34	1.92	11.25	2.44	7.12	1.20	7.00	1.17	0.80	37.70	37.00	72.00
C	2.2	935.8	62.1	63.3	145.4	14.62	53.8	11.3	2.06	10.39	1.68	10.59	2.03	6.37	1.05	6.02	0.96	1	40.5	64	77
C	1.8	615.6	75.5	72.8	170.9	16.52	58.8	12.7	2.35	11.9	1.95	12.27	2.45	7.7	1.09	7.08	1.1	0.8	42	66	137
PM7	2.00	1,762.80	65.60	56.00	126.60	13.92	52.50	11.00	2.00	9.25	1.60	10.67	2.33	6.69	1.16	7.64	1.28	4.10	55.80	61.00	248.00
D_EW	1.6	1091.2	52.3	36.8	96.2	10.63	36.8	8.2	1.58	7.56	1.38	7.81	1.75	5.1	0.75	4.66	0.87	2.2	46.1	24.8	92
D_RIVER RD	1.7	1412.2	66.7	45.4	115.3	12.52	43.5	9.8	1.77	8.73	1.62	10.82	2.19	6.39	0.99	6.59	1.04	1.3	44.7	44.7	155
I5	1.50	595.70	41.00	46.10	104.70	11.54	44.10	8.50	1.58	7.12	1.24	7.13	1.42	4.08	0.71	4.31	0.62	3.70	50.40	188.20	370.00
Earth	1.9	193	21	31	63	7.1	27	4.7	1	4	0.7	3.9	0.83	2.3	0.3	1.96	0.31	1.1	28	17	67
L1	1.20	973.10	59.20	62.50	141.70	15.06	55.50	12.00	2.04	10.31	1.78	9.78	2.13	6.01	0.96	6.01	0.99	1.00	36.80	44.50	78.00
L2	2.30	1,733.50	77.70	73.80	163.20	17.06	67.00	13.60	2.51	11.82	1.98	11.82	2.62	8.05	1.32	8.64	1.42	1.20	30.20	46.50	120.00
B4	2.10	600.50	48.10	42.30	92.80	10.19	38.40	8.00	1.52	7.07	1.36	7.21	1.64	4.68	0.77	4.64	0.71	1.40	33.80	27.20	68.00
B1	1.60	327.80	47.00	42.50	96.60	10.77	42.10	9.10	1.74	8.25	1.42	7.89	1.53	4.42	0.68	3.91	0.62	0.80	27.90	24.10	69.00
I	1.9	779.4	46.4	42.8	95.3	10.09	36.4	7.4	1.34	6.7	1.15	7.6	1.56	5.2	0.81	4.99	0.77	0.7	16.5	27.3	57
I	1.7	211	42.1	40.8	96.2	10.71	39	9.1	1.59	7.51	1.34	7.49	1.42	3.67	0.54	3.43	0.47	1.1	33.1	33.9	66
La	1.5	321	42.7	36.2	88.1	10.13	36.7	8.1	1.51	6.74	1.33	6.89	1.47	4.02	0.57	3.52	0.6	0.8	29.4	23.5	54
I_b	1.9	327.3	45.4	36.2	94.9	10.44	39.3	8.6	1.44	7.7	1.43	7.83	1.6	4.12	0.56	3.9	0.58	0.9	29.3	31.8	61
I_c	1.8	355.6	43.6	35.9	89.7	10.37	36.9	7.7	1.48	7.41	1.43	7.2	1.44	4.05	0.59	3.67	0.57	0.7	25	22.7	72
PM5	1.90	1,249.60	72.60	59.80	141.40	15.02	56.90	11.90	2.14	10.57	1.86	11.32	2.40	7.17	1.16	7.21	1.11	1.70	50.10	63.60	122.00
I4	2.00	1,039.10	48.90	50.60	111.70	12.64	49.50	10.50	1.77	10.02	1.52	9.71	1.86	5.90	0.86	5.74	0.91	2.90	58.50	119.30	346.00
I3	1.70	224.30	32.40	36.70	70.10	7.39	26.10	5.10	1.08	5.45	0.97	6.53	1.31	4.07	0.59	3.94	0.56	0.20	100.50	5.80	21.00
MSQUARE	2.1	379.1	58.4	84.5	138.2	20.05	77.2	15.9	2.93	13.16	1.99	10.67	2.11	6.02	0.86	5.28	0.84	0.9	85.6	25.8	110
I2	2.40	590.40	42.30	40.10	86.20	9.99	36.70	7.50	1.56	7.54	1.29	6.64	1.66	5.29	0.81	4.80	0.77	0.60	19.90	15.00	42.00
B2	2	821.6	45.6	43.1	95.5	10.36	39.7	8.5	1.44	7.73	1.3	7.83	1.53	4.83	0.78	4.67	0.76	0.9	17.8	14.4	47
O	2	863.5	49.7	36.4	82.5	8.95	34.1	7.5	1.36	7.35	1.26	8.49	1.71	5.49	0.84	5.57	0.84	0.8	26.3	56.2	110
O	2.3	477.3	41.8	37.8	82.1	9.33	35.9	6.9	1.35	6.21	1.02	6.81	1.37	4.12	0.7	4.03	0.65	0.8	20.1	70.7	36
P1	2.4	967.9	130.6	117.8	220.3	31.23	122.8	26.2	5.09	24.52	3.91	23.56	4.43	13.07	1.88	10.96	1.83	1	26.8	16.7	64
P	2.1	953.3	70.9	74.7	187.6	19.25	72.8	15.1	2.77	13.03	2.19	12.56	2.35	7.38	1.19	6.86	1.14	0.6	34.6	27.5	59
P_a	2	1003.5	122.1	92.5	200	28.2	108.1	22.5	4.32	21.14	4.14	20.75	4.31	11.07	1.73	10.19	1.58	0.6	27.3	16.4	61
P_b	1.8	759.5	55	53.1	128.4	14.19	50.5	10.1	1.69	8.21	1.72	9.58	1.98	5.57	0.89	5.45	0.88	0.7	27.9	18.1	57
P_c	1.9	723.6	49.3	46	109.2	12.51	42.5	8.5	1.44	6.78	1.42	7.93	1.67	4.47	0.72	4.65	0.8	0.6	17.8	17.2	39
B3	2.1	866.3	55.7	47.1	104.7	11.39	42.6	9.1	1.76	8.34	1.42	9.07	1.95	5.73	0.84	5.82	0.92	3	24.4	18.5	46
Q	1.8	592.8	52.2	46.3	101.1	11.25	41.5	8.5	1.72	8.36	1.45	6.77	1.75	5.42	0.83	5.33	0.75	0.6	25.7	37	67
Q	1.9	2162.4	76.1	51	127.4	14.33	49.8	9.7	1.83	9.78	1.93	11.17	2.67	7.79	1.2	7.65	1.32	1.2	58.1	39.4	149
Q	2.2	551.1	33.7	31.6	64.3	7.14	24.9	5.3	0.85	4.4	0.85	5.33	1.16	3.64	0.55	4.06	0.67	0.9	22.9	46.9	22
II	1.7	654.7	45.4	39.6	90.7	10.34	36.3	7.2	1.34	6.05	1.28	7.22	1.71	4.33	0.67	4.3	0.68	0.6	7.8	27.7	35
PU1	1.1	965.1	50.7	44.7	177.3	13.99	49.9	9.8	1.71	7	1.52	8.37	1.72	4.89	0.74	5.38	1.04	1.4	46.7	56.3	66
SE 10-22-05	2.1	374.1	46.4	49.8	112.2	12.55	49.3	9.8	1.65	8.56	1.28	7.99	1.55	4.61	0.77	4.48	0.65	2.7	87.7	63.3	392
SE 10-7-05	2.5	390.3	41.6	40.9	91.4	10.02	35.9	8	1.68	8.02	1.17	7.3	1.43	4.21	0.66	3.96	0.61	9	129.5	64.1	411
SE 1-18-06	1.7	397.3	45.3	40.4	99.6	11.67	41.5	9.1	1.57	7.43	1.43	7.88	1.53	4.14	0.58	4.06	0.6	1.9	114	55.1	291
SE 12-25-05	1.8	480.2	43.6	39.4	98.6	10.94	38.4	8.4	1.48	7.36	1.36	6.79	1.53	4.04	0.63	3.72	0.54	2	124.1	56.8	289
SE 2-9-06	1.9	545.5	45.6	37	92.9	10.42	39.2	7.8	1.38	7.27	1.29	7.7	1.46	4.2	0.59	3.94	0.54	1.4	74	46.2	194
SE 4-23-06	1.9	301.4	44.3	41.4	109.7	12.09	44.6	8.7	1.59	6.8	1.4	7.84	1.46	4.02	0.64	3.93	0.56	1.9	52.1	48	222
SE 5-11-06	2.2	411.8	40.5	34.8	87.7	9.93	37.3	8.2	1.42	6.52	1.25	7.04	1.35	3.78	0.55	3.41	0.58	3.1	94.9	70	390
SE 6-25-06	1.7	409.2	43.7	38	96.5	11.1	41.5	8.5	1.45	7.38	1.27	7.91	1.53	3.99	0.57	3.5	0.52	2.1	87.9	65.7	313
Stops near school	1.7	506.5	42.9	35.6	90	9.9	39.4	7.4	1.31	6.08	1.19	7.02	1.47	4.12	0.63	3.96	0.59	0.6	33.1	36.9	110
Street Residue Fall	1.1	841.3	42.2	30.3	83.3	8.94	34.7	6.9	1.09	5.8	1.03	6.87	1.32	3.91	0.61	3.63	0.69	2.8	96.7	92.4	290
Street Residue Spring	1.2	763.9	39.6	32.3	82	9.23	34.9	7.1	1.05	6.11	1	6.28	1.29	3.73	0.61	3.44	0.6	1.7	77.8	91.7	262
PU3	1.6	518.2	47	39.2	96	11.78	45.3	8.1	1.47	6.97	1.42	8.02	1.57	4.28	0.61	4.35	0.69	0.9	27	45.8	76
PU2	1.8	651.5	38.9	33.8	96.5	8.69	37.4	6.2	1.04	4.93	1.09	6.08	1.36	3.76	0.61	3.9	0.63	0.8	20.8	58.5	46
BU1	1.5	590	40.7	29.3	77.6	8.3	30.8	5.5	1.01	5.14	1.06	6.81	1.43	3.9	0.6	3.65	0.57	0.7	16.8	19.7	52
PMU2	1.3	579.1	41.5	33.9	85.9	9.12	32.1	6.8	1.23	6.75	1.26	6.9	1.43	4.26	0.59	4.14	0.57	0.8	21.1	107.2	107
IU1	1.9	480.7	36.9	33.9	82.6	8.91	36.1	5.9	1.03	5.01	0.97	5.36	1.33	3.54	0.58	3.4	0.58	0.5	16.8	30.5	55
PMU1	1.6	589.5	40.4	33.3	80.1	9.12	34.7	6.3	1.23	5.5	1.07	6.39	1.35	3.88	0.59	4.12	0.6	0.7	25.1	96.9	111
IU2	1.4	589.5	40.5	33.1	80.4	9.05	35.1	6.3	1.03	5.47	1.11	6.83	1.36	4.06	0.62	3.82	0.57	0.8	17.7	61.1	65

Site	Ni	As	Cd	Sb	Bi	Ag	Au	Hg	Tl	Se
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
A	33	4.1	0.3	0.2	0.3	0.1	1.9	0.07	0.2	0.5
P4	15.90	2.10	0.10	0.10	0.30	0.10	2.60	0.04	0.20	0.50
Pdump	25.1	7.8	4.3	2.3	0.8	0.7	86.2	1.71	0.2	0.5
P3	5.15	0.5	0.1	0.1	0.1	0.1	2.95	0.02	0.1	0.5
PM6	25.60	3.20	0.30	0.50	0.20	0.10	5.40	0.12	0.10	0.50
P2	19.50	3.70	0.20	1.10	0.30	0.20	6.30	0.08	0.20	0.50
C	21.9	4.1	0.2	0.4	0.4	0.5	0.7	0.12	0.3	0.8
C	34.4	3	0.4	0.5	0.3	0.2	0.6	0.14	0.4	0.9
PM7	44.70	5.00	0.80	1.00	0.20	0.20	6.30	0.18	0.10	0.50
D_EW	21.4	4.4	0.4	0.2	0.1	0.1	1.5	0.04	0.1	0.5
D_RIVER RD	31.9	4.7	0.3	0.4	0.2	0.1	2.1	0.11	0.1	0.5
I5	42.40	7.00	1.30	1.30	0.20	0.60	4.40	0.38	0.10	0.60
Earth	47	4.8	0.09	0.4	0.18	0.053	1.5	0.05	0.9	0.09
L1	21.90	2.60	0.40	0.20	0.30	0.10	6.00	0.07	0.20	0.60
L2	28.40	2.90	0.50	0.40	0.30	0.10	5.00	0.24	0.20	0.50
B4	17.60	3.60	0.20	0.30	0.10	0.60	3.40	0.09	0.10	0.50
B1	22.60	7.00	0.40	0.30	0.20	0.20	20.40	0.08	0.10	0.70
I	12.1	4.2	0.2	0.3	0.2	0.1	12	0.04	0.1	0.5
I	24.1	7	0.4	0.3	0.2	0.1	5.2	0.14	0.2	1.2
I_a	20.7	6.7	0.4	0.2	0.2	0.1	0.7	0.07	0.1	0.9
I_b	21.9	6.1	0.3	0.2	0.2	0.1	1.5	0.1	0.2	1
I_c	25.3	6.9	0.4	0.2	0.2	0.1	0.8	0.08	0.1	0.9
PM5	38.10	3.60	0.50	0.50	0.20	0.20	3.70	0.16	0.20	0.50
I4	45.00	6.40	0.80	0.80	0.30	0.40	2.70	0.10	0.10	1.00
I3	2.60	5.90	0.10	0.10	0.10	0.10	2.90	0.04	0.10	0.50
MSQUARE	53.7	0.6	0.1	0.1	0.4	0.1	0.9	0.02	0.4	0.5
I2	9.50	3.00	0.10	0.10	0.20	0.10	0.90	0.04	0.10	0.50
B2	11.4	3.8	0.1	0.2	0.2	0.1	0.5	0.04	0.1	0.5
O	17.3	3.4	0.5	0.5	0.1	0.1	1.2	0.05	0.1	0.5
O	7.8	4.3	0.1	0.5	0.2	0.1	7.3	0.08	0.1	0.5
P1	19.7	0.5	0.1	0.1	0.2	0.1	0.5	0.02	0.3	0.6
P	16.4	2.8	0.1	0.2	0.8	0.1	0.6	0.05	0.3	0.5
P_a	21.2	4.4	0.1	0.1	0.2	0.1	0.5	0.02	0.3	0.6
P_b	15.9	2.8	0.1	0.1	0.2	0.1	1.4	0.02	0.2	0.5
P_c	10.5	3.7	0.1	0.1	0.2	0.1	0.5	0.02	0.2	0.5
B3	16.4	4	0.2	0.2	0.1	0.1	0.5	0.04	0.1	0.5
Q	19.6	3.3	0.2	0.4	0.2	0.1	1.1	0.08	0.2	0.5
Q	30.7	4.1	0.3	0.4	0.2	0.2	1.1	0.25	0.1	0.5
Q	5.7	5.1	0.1	0.6	0.2	0.1	2.4	0.1	0.1	0.8
I1	7.9	2.7	0.1	0.1	0.1	0.1	0.5	0.05	0.1	0.5
PU1	24.7	3.3	0.2	0.2	0.5	0.1	3.8	0.09	0.3	0.6
SE 10-22-05	56	4.9	4.3	0.9	0.2	0.4	9.1	0.23	0.2	0.6
SE 10-7-05	75.1	5.5	10.8	1.9	0.3	0.2	4.6	0.14	0.2	0.7
SE 1-18-06	43.9	6.1	2.3	1.2	0.3	0.2	3.5	0.2	0.2	0.6
SE 12-25-05	41.9	6.1	3	1.3	0.3	0.4	7.5	0.28	0.2	0.6
SE 2-9-06	30.7	5.7	0.7	1	0.2	0.1	6.2	0.12	0.1	0.6
SE 4-23-06	35.2	5.9	1.4	0.4	0.2	0.2	21.1	0.18	0.2	0.7
SE 5-11-06	55.7	5.8	1.9	1.2	0.5	0.4	11.9	0.26	0.2	0.7
SE 6-26-06	46.8	7.2	0.8	0.9	0.3	0.2	9.1	0.16	0.2	0.5
Slopesnearschool	21.1	5.8	0.2	0.2	0.2	0.1	2.1	0.06	0.1	0.5
Street Residue Fall	40.6	4.6	1	2.4	0.3	0.1	3.3	0.1	0.1	0.5
Street Residue Spring	46.1	4	0.7	1.4	0.3	0.2	8.4	0.11	0.1	0.5
PU3	12.9	4.7	0.5	0.2	0.4	0.7	9.4	0.1	0.2	0.8
PU2	10.9	5	0.1	0.3	0.5	0.1	1	0.11	0.2	0.9
BU1	17.6	4	0.1	0.1	0.1	0.1	0.9	0.03	0.1	0.6
PMU2	11.7	4.3	0.3	0.3	0.2	0.1	2.4	0.1	0.1	0.5
IU1	9.7	3.2	0.2	0.1	0.3	0.1	0.7	0.11	0.2	0.5
PMU1	12	3.8	0.4	0.6	0.2	0.1	1.7	0.09	0.1	0.5
IU2	13.3	3.8	0.1	0.4	0.2	0.2	2.5	0.06	0.1	0.6

## Appendix D: Detection Limits

Detection limits for trace elements

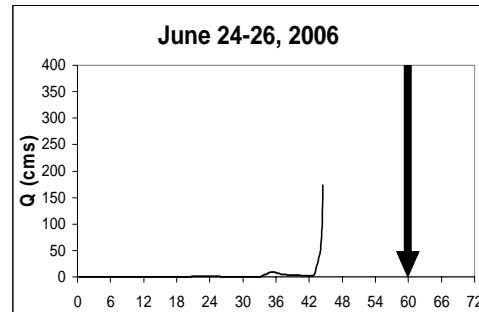
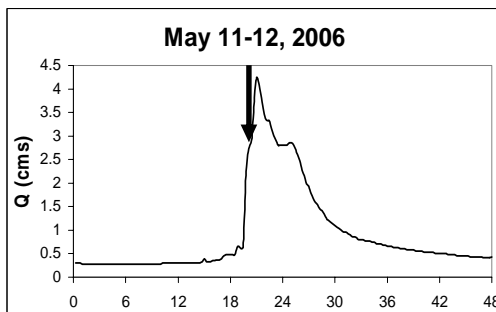
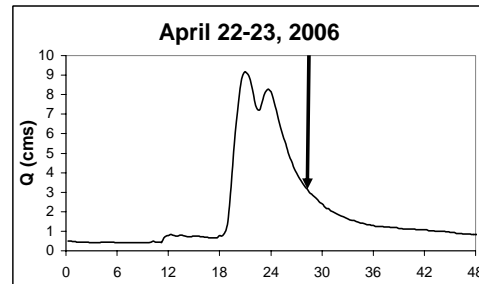
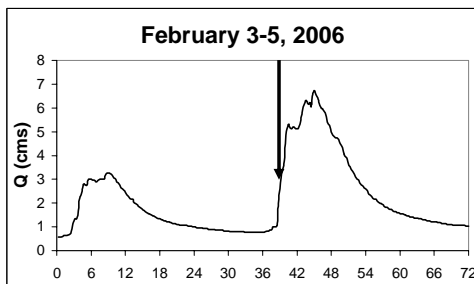
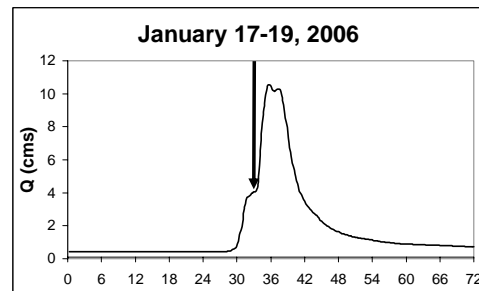
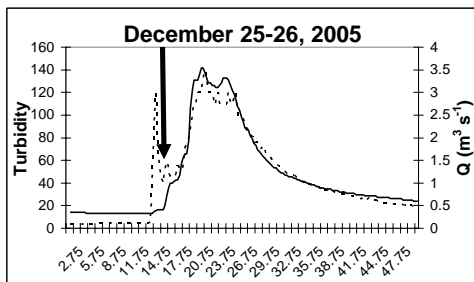
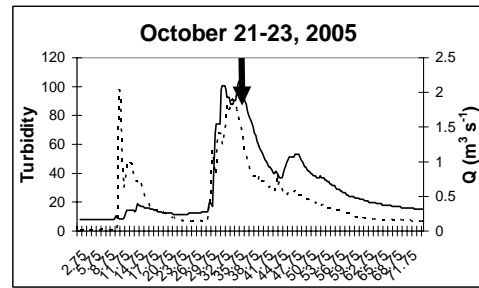
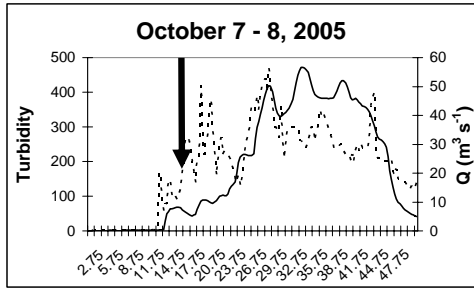
	Det. Lim.	Det. Lim.	Limit
SiO <sub>2</sub>	0.04 %	-	100 %
Al <sub>2</sub> O <sub>3</sub>	0.03 %	-	100 %
Fe <sub>2</sub> O <sub>3</sub>	0.04 %	-	100 %
CaO	0.01 %	-	100 %
MgO	0.01 %	-	100 %
Na <sub>2</sub> O	0.01 %	-	100 %
K <sub>2</sub> O	0.04 %	-	100 %
MnO	0.01 %	-	100 %
TiO <sub>2</sub>	0.01 %	-	100 %
P <sub>2</sub> O <sub>5</sub>	0.01 %	-	100 %
Cr <sub>2</sub> O <sub>3</sub>	0.001 %	-	100 %
LOI	0.1 %	-	100 %
C	0.01 %	-	100 %
S	0.01 %	-	100 %
Au	-	0.5 ppb	100 ppm
Ag	-	0.1 ppm	100 ppm
As	-	1 ppm	10000 ppm
Ba	5 ppm	0.5 ppm	50000 ppm
Be	-	1 ppm	10000 ppm
Bi	-	0.1 ppm	2000 ppm
Cd	-	0.1 ppm	2000 ppm
Co	20 ppm*	0.5 ppm	10000 ppm
Cs	-	0.1 ppm	10000 ppm
Cu	20 ppm*	0.1 ppm	10000 ppm
Ga	-	0.5 ppm	10000 ppm
Hf	-	0.5 ppm	10000 ppm
Hg	-	0.1 ppm	100 ppm
Mo	-	0.1 ppm	2000 ppm
Nb	20 ppm*	0.5 ppm	50000 ppm
Ni	20 ppm	0.1 ppm	10000 ppm
Pb	-	0.1 ppm	10000 ppm
Rb	-	0.5 ppm	10000 ppm
Sb	-	0.1 ppm	2000 ppm
Sc	1 ppm	-	10000 ppm
Se	-	0.5 ppm	100 ppm
Sn	-	1 ppm	10000 ppm
Sr	10 ppm	0.5 ppm	50000 ppm
Ta	20 ppm*	0.1 ppm	50000 ppm
Th	-	0.1 ppm	10000 ppm
Tl	-	0.1 ppm	1000 ppm
U	-	0.1 ppm	10000 ppm
V	-	5 ppm	10000 ppm
W	-	0.1 ppm	10000 ppm
Y	10 ppm	0.1 ppm	50000 ppm
Zn	20 ppm*	1 ppm	10000 ppm
Zr	10 ppm	0.5 ppm	50000 ppm
La	-	0.5 ppm	50000 ppm
Ce	20 ppm*	0.5 ppm	50000 ppm
Pr	-	0.02 ppm	10000 ppm
Nd	-	0.4 ppm	10000 ppm
Sm	-	0.1 ppm	10000 ppm
Eu	-	0.05 ppm	10000 ppm
Gd	-	0.05 ppm	10000 ppm
Tb	-	0.01 ppm	10000 ppm
Dy	-	0.05 ppm	10000 ppm
Ho	-	0.05 ppm	10000 ppm
Er	-	0.05 ppm	10000 ppm
Tm	-	0.05 ppm	10000 ppm
Yb	-	0.05 ppm	10000 ppm
Lu	-	0.01 ppm	10000 ppm

Detection Limits for Radionuclides

Cs-137 - 1.0 Bq kg<sup>-1</sup>

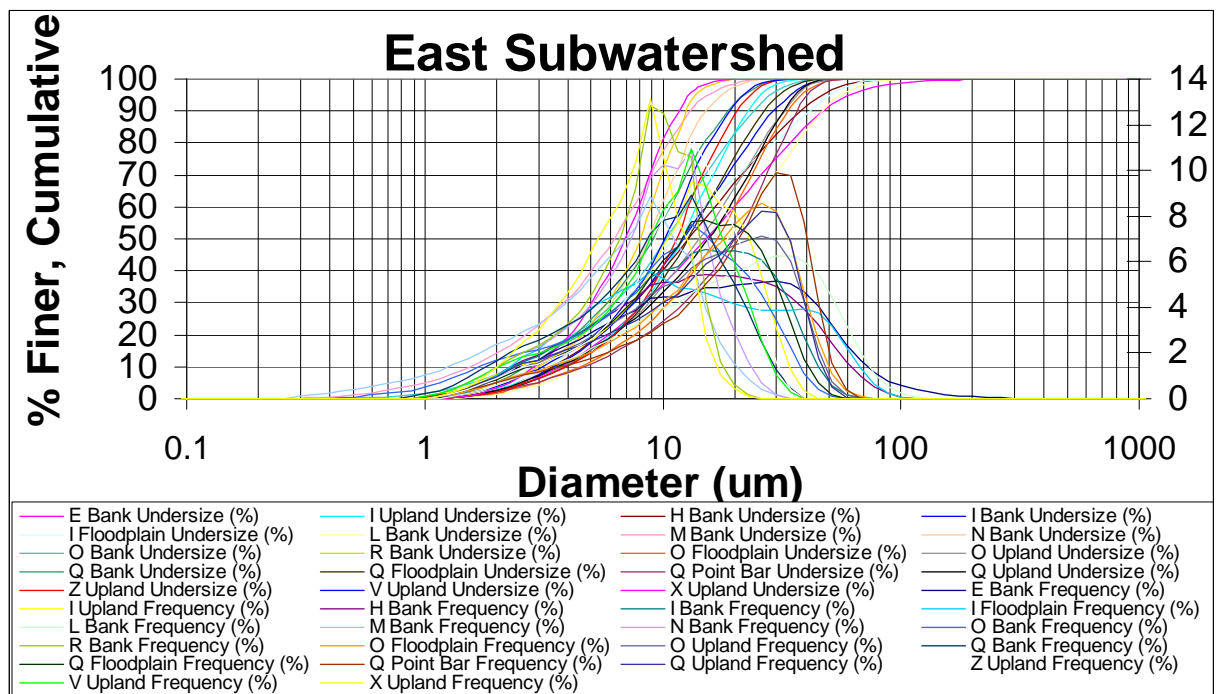
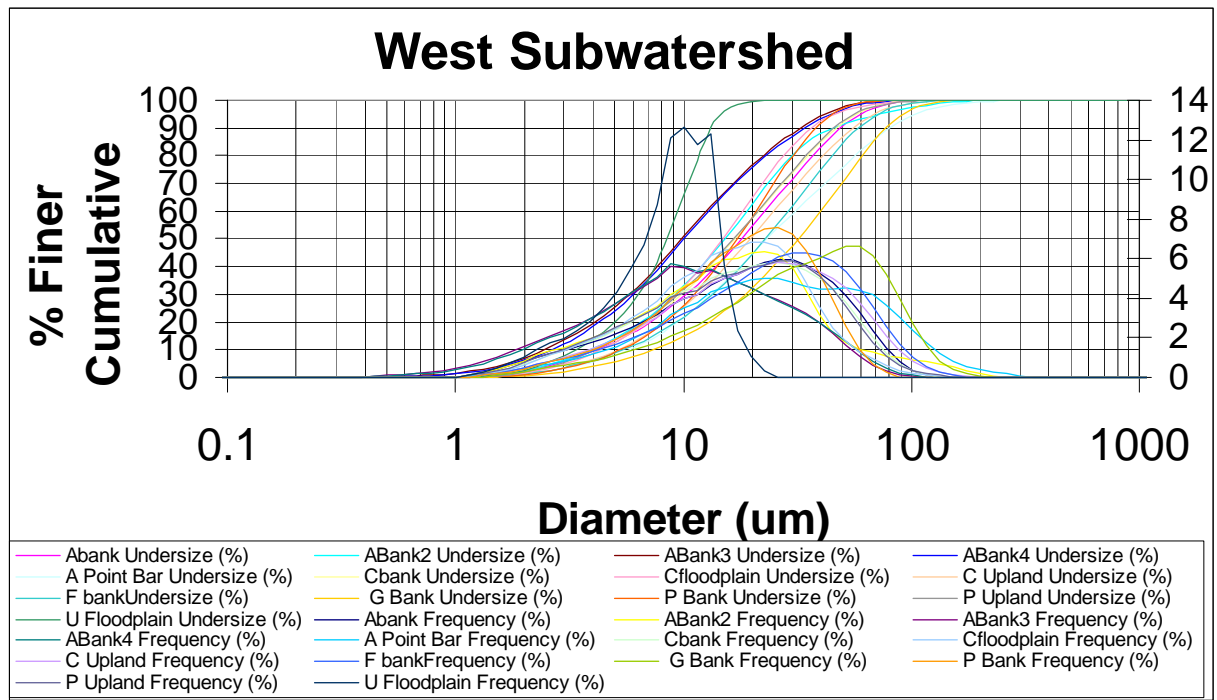
K-40 - 10.0 Bq kg<sup>-1</sup>

## Appendix E: Sedigraphs and Hydrographs for Suspended Sediment Sample Collection Times

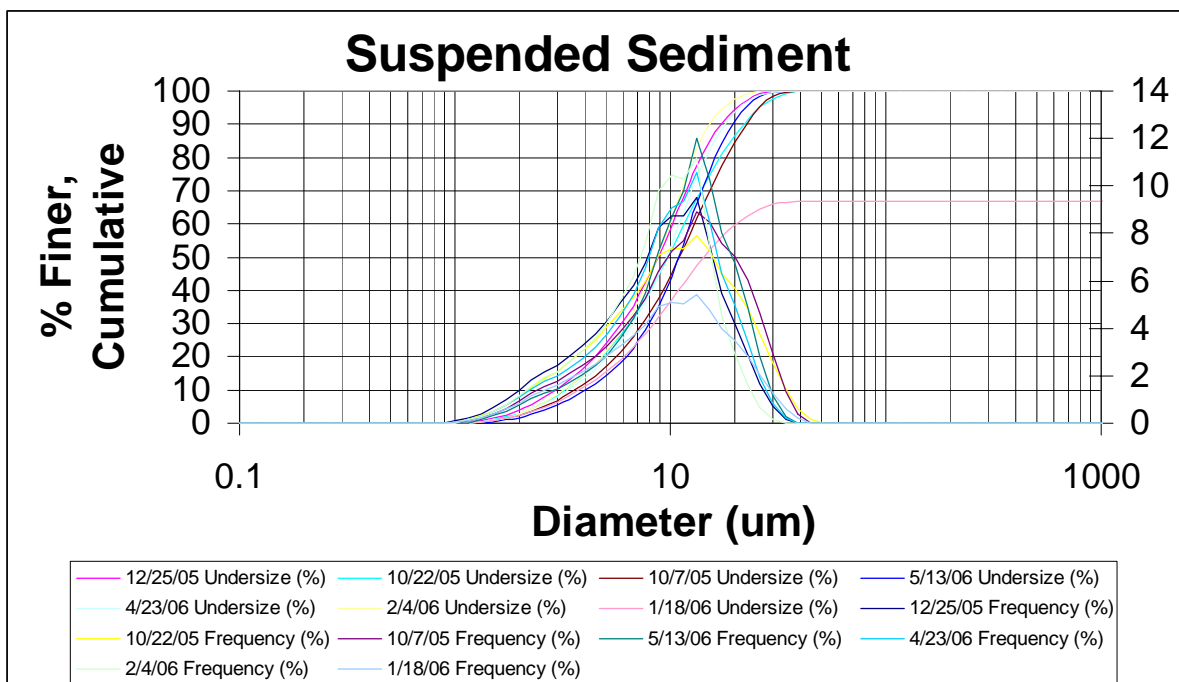


The x-axis is hours. Note the y-axis varies depending on storm size. The dashed line is turbidity measured as monochrome near infra-red LED light, 780-900 nm, detection angle  $90 \pm 2.5$  degrees. The solid line is discharge.

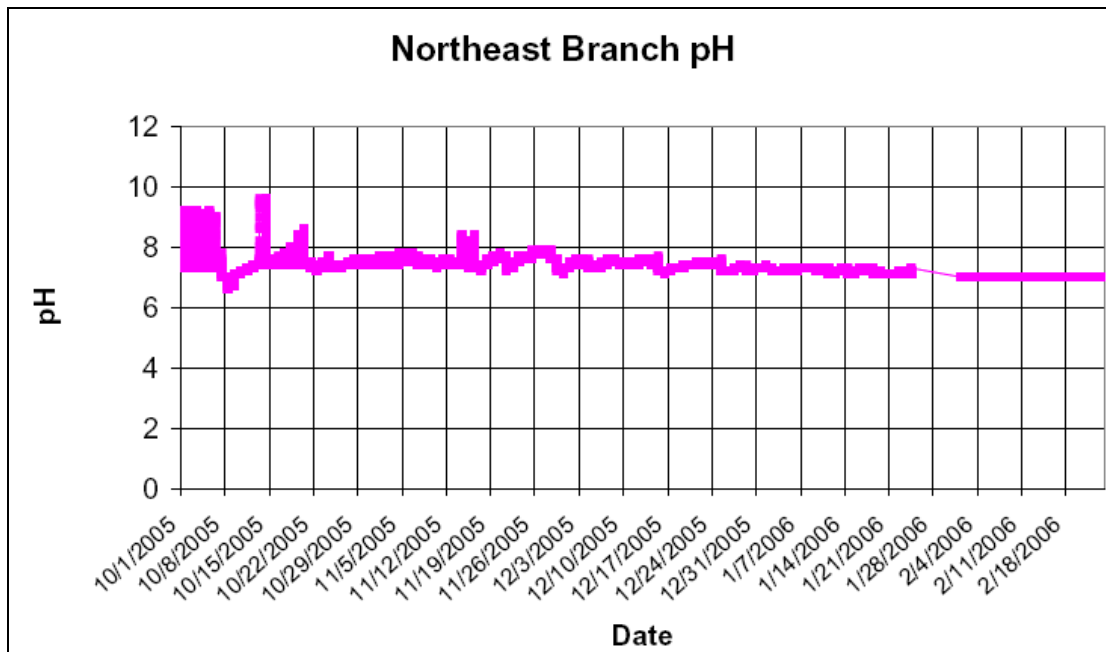
## Appendix F: Particle-Size Distributions







## Appendix G: pH data



Source: USGS, Maryland Water Science Center, USGS 01649500 North East Branch Anacostia River at Riverdale, MD, <http://waterdata.usgs.gov/md/nwis/>.

## Appendix H: Periodic Table

# Periodic Table of Elements

Representative elements

Alkali metals  
↓  
Group 1A

Alkaline earth metals  
↓  
Group 2A

Period number	1	2	Transition elements										13	14	15	16	17	18
	Group 1A	Group 2A		3B	4B	5B	6B	7B	8B	1B	2B	Group 3A	Group 4A	Group 5A	Group 6A	Group 7A	Group 8A	
1	1 H 1.008																2 He 4.003	
2	3 Li 6.941	4 Be 9.012										5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18	
3	11 Na 22.99	12 Mg 24.31										13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95	
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57* La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209	85 At 210	86 Rn 222
7	87 Fr 223	88 Ra 226	89† Ac 227	104 Rf 261	105 Db 262	106 Sg 263	107 Bh 262	108 Hs 265	109 Mt 266	110 — 269	111 — 272	112 — 277	113 — 284	114 — 289	115 — 288	116 — 289	117 — 289	118 — 289

Halogens  
↓  
Group 7A

Noble gases  
↓  
Group 8A

\*Lanthanides

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 145	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
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†Actinides

90 Th 232.0	91 Pa 231	92 U 238.0	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260
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Metals

Metalloids

Nonmetals

(<http://universe-review.ca/index.htm>, 2006)

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