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Mercury Contamination Of Channel And Floodplain Sediments In Wilson Creek Watershed, Southwest Missouri

Willard E. Rodgers II
Missouri State University

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**MERCURY CONTAMINATION OF CHANNEL AND FLOODPLAIN
SEDIMENTS IN WILSON CREEK WATERSHED, SOUTHWEST MISSOURI**

A Thesis

Presented to

The Graduate College of
Southwest Missouri State University

In Partial Fulfillment

Of The Requirements for the Degree

Master of Science, Geospatial Science: Physical Geography

By

Willard Eugene Rodgers II

May 2005

MERCURY CONTAMINATION OF CHANNEL AND FLOODPLAIN SEDIMENTS IN WILSON CREEK WATERSHED, SOUTHWEST MISSOURI

Department of Geography Geology and Planning

Southwest Missouri State University, May 2005

Master of Science, Geospatial Science: Physical Geography

Willard Eugene Rodgers II

ABSTRACT

Mercury (Hg) is a pollutant affecting aquatic environments and human health world wide. Sediments in urban streams can store Hg from historical industrial waste releases in channel and floodplain deposits. Subsequent erosion of these deposits can remobilize sediment-bound Hg impacting downstream receiving waters. This study describes the distribution of Hg in floodplain and channel sediments of Wilson Creek and its tributaries using geochemical sediment analysis and cesium-137 dating. The upper Wilson Creek watershed drains the southern two-thirds of Springfield, Missouri. Results indicate that Hg concentrations in overbank and active channel sediments along the entire stream length are elevated above the mean background level of 20 ppb measured in pre-settlement overbank deposits. Background Hg levels are possibly associated with organic and iron content in these deposits. Historically-contaminated post-settlement overbank deposits are ~ 1 m thick with sedimentation rates ranging from 0.5 to 1 cm per year. In the upper watershed, these deposits have Hg contamination deep in the overbank profile. Mercury stored in these deposits serves as a nonpoint source to channel sediments as indicated by a contamination trend originating within the historical industrial center. This trend reaches a peak concentration of 1,240 ppb Hg downstream of a closed waste water treatment plant and landfill site. In the lower watershed, historically contaminated sediment combines with recent mercury releases to produce a second trend characteristic of both nonpoint and point source releases. This trend reaches 1,940 ppb Hg downstream of two municipal utility facilities. Surface to stream karst connections complicate source identification in the lower watershed. Even with current reductions in the use and emission of mercury, historically contaminated sediment stored within the Wilson Creek watershed may be a source of Hg to receiving waters for decades to centuries.

KEYWORDS: mercury, fluvial sediments, Wilson Creek, Springfield, urban pollution

This abstract is approved as to form and content

Dr. Robert Pavlowsky
Chairperson, Advisory Committee
Southwest Missouri State University

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Approved:

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CHAPTER ONE:

INTRODUCTION

SEDIMENT SURVEYS TO ASSESS WATER QUALITY

Non-point source pollution assessments have begun to incorporate the use of watershed-scale analysis of sediment yields and geochemistry to understand human impacts on river systems (USEPA, 1995; James, 2004). The geographical concepts of fluvial sedimentation processes have long been adapted and applied to human-related disturbances within drainage basins (Gilbert, 1917; Strahler, 1956; Knox, 1977; Graf, 1996). Combining geochemical sediment quality assessment with an understanding of watershed-scale sediment dynamics is useful in describing the downstream distribution of pollutants within urban stream systems since toxic pollutants can be incorporated in or sorb to sediment particles (Forstner and Whitmann, 1981; Horowitz, 1991). It is the concentrations of these sediment-bound pollutants that is the target of geochemical analysis.

Previously, the investigation, assessment, and monitoring of aquatic environment “health” has focused mainly upon the quality of the water within the system. Water quality is typically measured through analytical chemical analysis of water samples, providing information on the water’s characteristics as a solvent and on total and dissolved pollutant levels at the moment and location of sample capture (Horowitz, 1991). A more holistic, or comprehensive, approach has been recently applied whereby pollutant concentrations are measured in the biota, the principle media of concern, and in the sediment – the major pollutant sink and reservoir in river systems (Horowitz, 1991; Forstner and Whitman, 1981). Incorporating sediment quality assessments into

comprehensive water quality studies is based upon the concept that aquatic sediments reflect the chemical, physical, and biological properties of the overlying water (Power and Chapman, 1992; USEPA, 1987).

Geochemical analysis of channel and floodplain sediment provides spatial and temporal information about the concentration, distribution, and sources of sediment-bound pollutants within the system. Mercury and other toxic metals can be adsorbed on finely-divided organic material, clay surfaces, iron and manganese oxides, and sulfides, incorporated into geochemical phases, and precipitated with calcium and magnesium carbonates. The presence of these geochemical substrates affect pollutant solubility, transport, and bioavailability and are indicated by the amounts of organic matter (OM), aluminum (Al), iron (Fe), manganese (Mn), sulfur (S), calcium (Ca), and magnesium (Mg) in the sediment (Forstner and Wittmann, 1981; Gabriel and Williamson, 2003).

Physical properties of the contaminated sediment, such as particle size, shape, and surface area, also affect adsorption and the spatial sorting of fine-grained pollutant deposition (Pavlowsky, 1995; Horowitz, 1991). This hydraulic sorting occurs as gravel, sand, and coarse silt particles are readily deposited during most flow conditions, while fine silt and clay-sized sediment fractions, and associated pollutants, remain in suspension or are deposited in zones of flow resistance. In an undisturbed stream, this general pattern of vertical and horizontal fining causes alluvial deposits to become finer in the downstream, vertical or upward, and lateral or cross-valley directions. (Lecce and Pavlowsky, 2001).

Generally, fluvial sediment assessment can provide information at two distinct temporal scales: recent time by evaluating active channel sediments, and the historical

period by studying in stratigraphic profiles in floodplain deposits. Fine-grained sediments stored at or below bankfull depth, the discharge stage associated with the most effective sediment transport, are considered active channel sediments reflecting recent source and transport trends. These deposits are typically remobilized by increased flows on a seasonal to annual time scale (Sweet and Geratz, 2003). Pollutants bound to these sediments are also similarly mobilized and are eventually transported out of the system or stored on the adjacent floodplain at the decade-scale. Contaminated fine-grained sediments in floodplain deposits are stored for longer periods of time and can be remobilized at the century-scale or longer by bank erosion during floods (Schumm, 1972; Novotny and Chesters, 1989) or by geochemical weathering and leaching (Faure, 1991). Common to areas of increased human activity, channels that are incised, enlarged, or engineered can contain relatively high discharge flows that effectively ends overbank deposition and reduces the potential for sediment deposition and pollutant storage in overbank deposits (Lecce and Pavlowsky, 2001). For channels that remain in this state, previously stored overbank sediment have reached a terminal sink if bank erosion rates are also reduced. The chemical stratigraphy of these deposits can therefore provide information about background pollutant levels, historic trends, and sedimentation rates (Horowitz, 1991; Lecce and Pavlowsky, 2001). Thus, an understanding of historical deposition patterns and local flood hydrology is essential in protecting long-term water quality within a basin (James, 2004).

The rate at which the pollutants are exported from the watershed or decrease in concentration downstream depends on several factors including: (1) dilution by cleaner sediment from tributary inputs or bank erosion, (2) deposition of contaminated sediment

in the channel or on the floodplain , (3) uptake of dissolved pollutants by biota, and (4) geochemical binding by sorption or precipitation. The introduction of uncontaminated sediment from tributary, bank, or land surface sources can dilute downstream pollutant concentration in the active channel sediment. Contaminated sediment mobilized during high flow events can “jump” to downstream channel deposits (Piest et al.,1975) or be stored in overbank floodplain deposits for longer time scales (Novotny and Chesters, 1989). The incorporation of mercury into plant and animal tissue also represents a temporary removal of mercury from channel deposits (USGS, 2001). However, considering the mobility of some animals, mercury stored in the biota is not necessarily removed to downstream locations. Finally, aging geochemical substrates, such as iron and manganese oxides in active channel sediment, can release mercury to solution for downstream transport (Waslenchuk, 1975).

The reduction of mercury in active channel sediment deposits by these factors has been observed to occur in a predictable manner and described as distance or longitudinal decay. Rose et al. (1970) used a multiple regression analysis step-wise procedure to identify key factors in downstream zinc and copper reduction. Hawkes (1976) predicted upstream copper ore grade and mineralization area using a downstream decay formula. Phillips (1988) utilized the spatial relationships between source location and distance decay relationships to develop a probability based risk assessment model. Thus, downstream dilution of pollutant concentrations produce trends revealing information about watershed-scale geomorphic sedimentation controls and pollutant source regions.

For resource managers who seek pollution information that provides the greatest utility, given limited financial resources and time, geochemical sediment assessment

provides definite advantages over conventional water sample analysis (Power and Chapman, 1992). Active channel and overbank deposits provide a time averaged sample medium of pollutant concentrations, whereas water samples offer only a snapshot of pollutant levels. In addition, many pollutants such as mercury have very low solubility and strong affinity for sediment, being stored predominantly in sediment deposits. Therefore, pollutant concentrations in the water may reveal less information about pollutant levels in the river system than those measured in sediments.

MERCURY IN WILSON CREEK

Mercury is now considered one of the most toxic and pervasive pollutants in aquatic environments world-wide and is responsible for the largest increases in fish consumption advisories in the U.S. since 1993 (Krabbenhoft et al., 1999; UNEP, 2002; USEPA, 2003). Natural chemical and physical weathering, volcanism, geothermal emissions, and volatilization from the oceans result in average mercury concentrations of 40 parts per billion (ppb) in carbonate bedrock formations and 10 to 100 ppb in soils (Forstner and Wittmann, 1981). Each year in the U.S. approximately 158 tons of mercury are released to the environment by anthropogenic sources including: the burning of fossil fuels, chlor-alkali plants, metal processing industry, medical and other waste incineration, pulp and paper industry, gold and mercury mining, municipal effluents, land application of sewage materials, and leaching of surface and buried consumer solid waste (Smol, 2002; USEPA, 2000). Natural processes and anthropogenic activity introduce mercury compounds into a complex global cycle involving storage and transportation within the atmosphere, natural waters, soil, and sediment (Smol, 2002; MDNR, 2002; USEPA, 2001). The storage and transport of mercury in local aquatic systems can be

investigated through the geochemical analysis of mercury sinks and reservoirs in channel and overbank sediment deposits of river systems (Forstner and Whitman, 1981; Horowitz, 1991; Pinsker, 2003).

All streams and lakes in Missouri are under a mercury-related fish consumption advisory (USEPA, 2003). Atmospheric emissions from coal burning power plants are considered the primary sources of mercury to most streams in the state. However, contaminated sediment from past releases of mercury-containing industrial wastes may be a substantial source to streams flowing through urban areas. Wilson Creek (218 km²) drains approximately two-thirds of the city Springfield, an urban center within the Ozarks region of Missouri (Figure 1). The upper portion of the Wilson Creek watershed that is most affected by urban and industrial discharges is drained by its main tributary, Jordan Creek (approximately 35 km²). Toxicity in Wilson Creek is documented as being from urban non-point sources of an unknown pollutant, evidenced by very low fish diversity and aquatic invertebrate animals (MDNR, 2002). Elevated levels of phosphorus (P), copper (Cu), lead (Pb), and zinc (Zn), as well as mercury are problematic in the watershed (Pierce, 1992; Black, 1997; Shade, 2003). Mercury has been detected in Wilson Creek water and sediment yet no watershed scale assessment of mercury sources or contamination has been conducted. The creek is one of the largest tributaries of the James River, whose waters empty into Table Rock Lake (Figure 2). All three water bodies are included on the EPA's 303 (d) list of impaired waterways (MDNR, 2002).

Historical industrialization-era manufacturing and metal processing plants within Springfield relied upon Jordan Creek to transport their waste water discharges

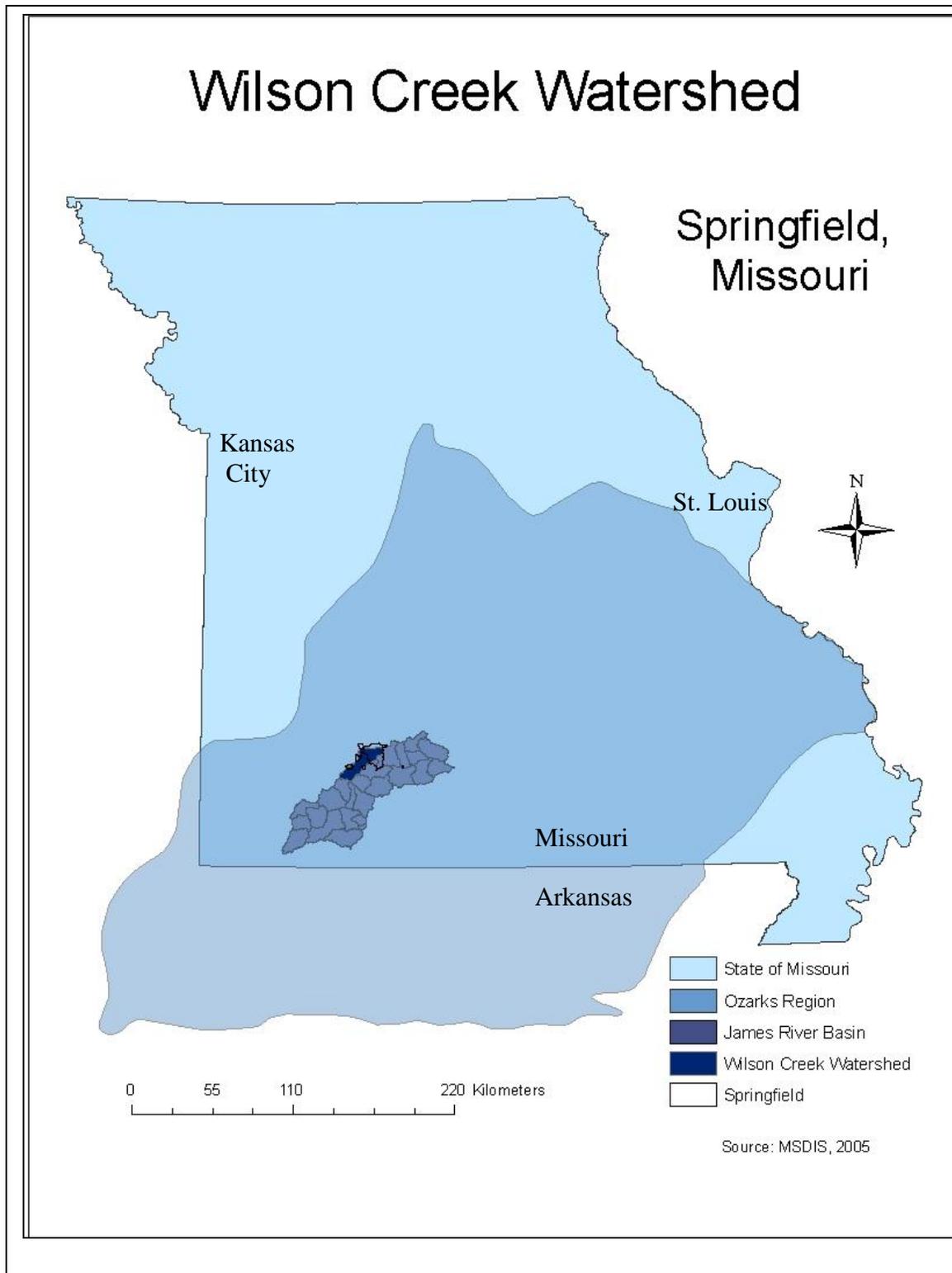


Figure 1. Regional location within the Ozarks of Missouri.

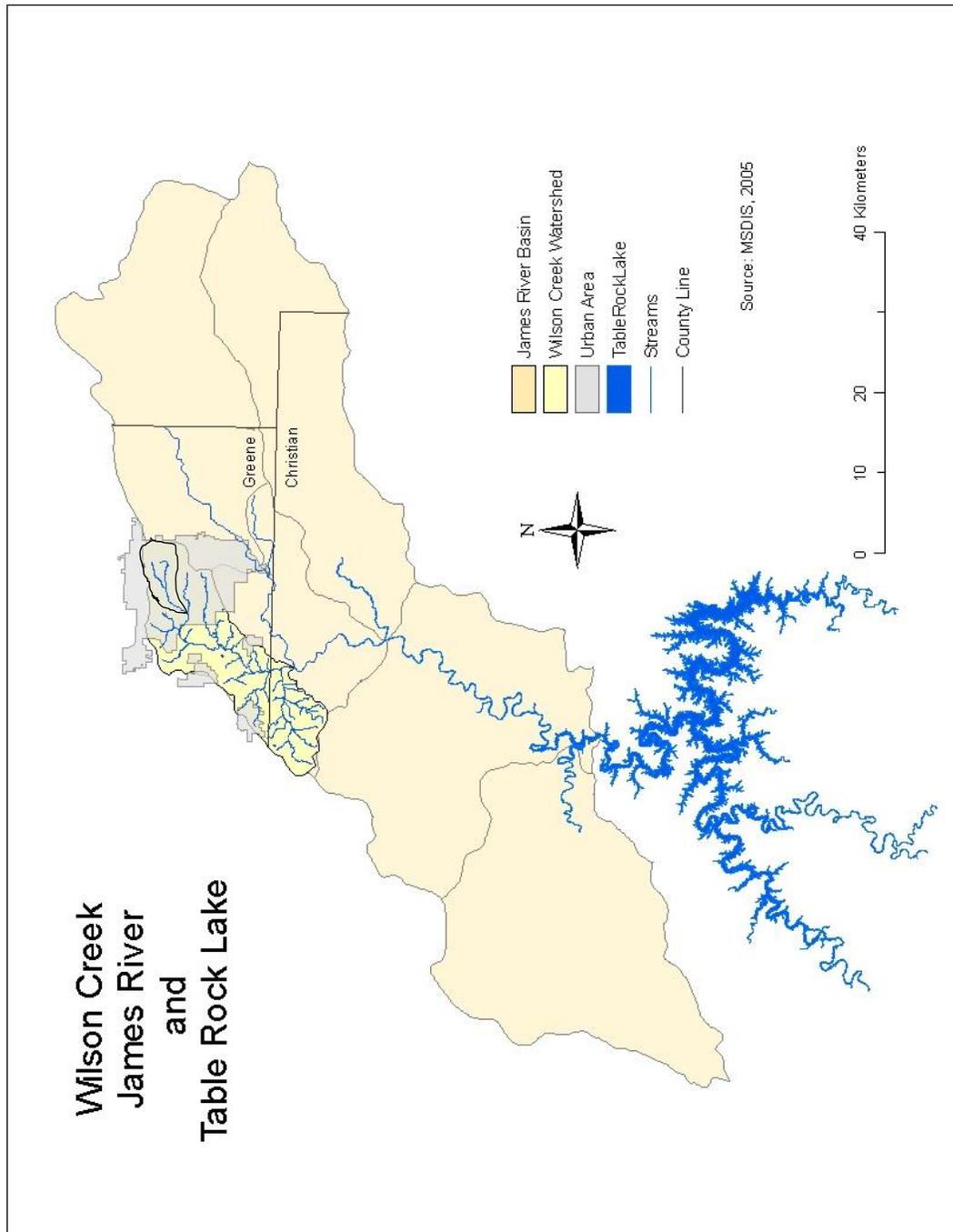


Figure 2. James River Basin and Table Rock Lake.

downstream (Shade, 2003). Mercury discharged to the stream was likely incorporated into the bed sediment and temporarily deposited in channel and overbank environments within the watershed. These stored sediments may act as nonpoint pollutant sources when they are eroded and remobilized during high discharge storm events (Trimble, 2001). Runoff of mercury-containing pesticides and sewage sludge soil conditioners applied to agricultural land surfaces in the past may contribute mercury to lower watershed reaches. Other mercury sources in the lower watershed include the Springfield Southwest Waste Water Treatment Plant (SW WWTP) and the Springfield Southwest Power Station (SWPS) which currently have permits to discharge mercury to Wilson Creek and two of its tributaries, respectively (Shade, 2003). The SWPS, adjacent to Wilson Creek, reported the release of 92 pounds of mercury compounds to the environment in 2002 (USEPA, 2004).

Mercury has been measured downstream of the SW WWTP and the SWPS in water, fish and sediment. Elevated levels of mercury were found in Wilson Creek water samples collected downstream of the SW WWTP in the early 1990's during routine sampling conducted by the city of Springfield (Barnes, 1995). Fish tissue samples (n = 7) collected in Wilson Creek by the Missouri Department of Conservation (MDC) and Department of Natural Resources (MDNR) between 1986 and 2002 as part of the state-wide EPA-mandated monitoring projects, contained mercury ranging from 30 to 280 ppb at sites in the lower watershed (Burdge, 2005). One channel sediment sample collected in the lower watershed in 1997 by MDNR contained 421 ppb mercury (Burdge, 2005). Average mercury concentrations enriched nine times background levels were measured in overbank sediment 3.2 km from the James River Confluence (Shade, 2003).

PURPOSE AND OBJECTIVES

The purpose of this study is to perform an exploratory geochemical survey of the active channel and overbank floodplain deposits of Wilson Creek and selected tributaries to determine the spatial and temporal distribution of sediment-bound mercury within the watershed.

The reduction and control of mercury loading to James River and Table Rock Lake is important for the economic well being of this tourism-dependant region of the Ozarks. The proposed regulation of atmospheric sources may not yield immediate reductions in mercury levels if historically contaminated sediment from upstream sources exist. Information regarding the distribution of mercury in the upstream the sediment sinks of Wilson Creek is essential for resource managers to identify mercury sources, accurately assess long-term contamination potential, and evaluate the effectiveness of regulatory actions. Two primary questions must be answered to assess source and longevity concerns related to mercury contamination in the James River and Table Rock Lake:

- 1) Is historical industrialization-era mercury stored in the channel and floodplain sedimentary deposits along Wilson Creek?

If so, what is the level and spatial distribution of contamination?

- 2) Is historical industrialization-era mercury or mercury from more recent urban sources actively being transported through the system?

If so, can mercury trends be linked to specific sources within the watershed?

This will be accomplished by three objectives.

- 1) Determine the spatial distribution of mercury and other pollutants (P, Cu, Pb, Zn) in the active channel sediments of Wilson Creek and selected tributaries. This information will be used to evaluate the present-day transport of mercury within Wilson Creek.
- 2) Determine the spatial and temporal distribution of mercury and other pollutants in overbank floodplain deposits throughout the watershed. This information will be used to understand historical pollution sources, storage locations, and background levels of sampled pollutants. Sediment layers will be dated by ^{137}Cs , with peak activity indicating a 1964 surface, and by the pre-settlement buried soil indicating approximately the 1850 surface.
- 3) Describe mercury pollution patterns at the watershed-scale using geochemical substrate and spatial decay models. This information will help identify the timing and location of sources, as well as the degree of mercury remobilization within Wilson Creek.

HYPOTHESES

The distribution of sediment-bound mercury in the active channel sediments of Wilson Creek is dependant upon the location of sources, the type and concentration of geochemical substrates, the role of geomorphic controls on sedimentation, and the amount and distribution of mercury stored in overbank deposits. It is expected that

historical contaminated bank and bed sediment is stored along the length of the stream and serves as non-point sources of mercury. Point sources in the lower watershed are expected to exist near the two municipal utility plants.

Hypothesis 1 – Geochemical and Sedimentological Controls

It is expected that organic matter, iron and aluminum will be closely associated with elevated levels of mercury and other pollutants throughout the watershed and among channel and overbank deposits. Organic matter and iron should prove important geochemical substrates responsible for adsorbing pollutants and affecting transport and storage fate. The effects of grain-size sorting should be reflected in aluminum – pollutant associations, with silt and clay sized overbank deposits containing more mercury and possibly displaying slightly stronger relationships than coarser channel deposits.

Hypothesis 2 – Spatial Distribution of Mercury

It is expected that historical overbank deposits will have elevated levels of mercury and other pollutants deeper in the profile in the upper watershed and closer to the floodplain surface in the lower watershed. Frequent upper watershed flooding in Jordan Creek before channelization and bank stabilization measures will have facilitated rapid local deposition of contaminated sediment on the historical floodplain surface near industrialization-era sources. If point and nonpoint mercury inputs are associated with more recent lower watershed sources such as the waste water treatment plant or power plant, then upper profile overbank deposits will be more contaminated in the lower watershed. Pollutant concentrations below historical deposits are expected to reflect regional background levels.

If lower watershed mercury sources are more prominent now, the active channel sediment mercury trend should display downstream attenuation from weak and diffuse sources in the upper watershed. Mercury releases in the upper watershed should be small owing to the potential lack of recent mercury inputs and reduced bank and bed sediment availability due to channel stabilization structures. Higher concentrations should be measured in the lower watershed near potential recent sources of mercury.

STUDY BENEFITS

Sediment investigations within the hydrologically unique Ozark streams of the Springfield Plateau have been conducted for certain trace elements (Mantei and Foster, 1991; Pierce, 1992; Mantei and Sappington, 1994; Gutierrez et al., 2004). These reach-scale studies have been instrumental in isolating point and non-point pollution sources, facilitating understanding trace metal transport in karst areas, and indicating areas of elevated pollutant levels for biological monitoring (Havel and Talbott, 1994). This watershed-scale mercury reconnaissance will have similar benefits on a larger scale, and for a toxic element whose distribution is heretofore unknown. Benefits to the scientific community should be realized through a better understanding of sediment-mercury storage and transport processes in this unique karstic fluvial environment. In addition, the establishment of a regional background level for mercury as seen in the lower overbank profile or pre-settlement deposits should be useful to those involved in investigating mercury in the Ozarks.

Mercury levels in the receiving waters of Wilson Creek will continue to be of interest until consumption advisories have been lifted. This study's watershed scale sediment-

mercury reconnaissance will provide local resource and storm water managers with valuable information with which to take meaningful action to reduce mercury bioavailability in downstream aquatic environments. For example, recognizing the mercury methylation potential of wetland environments (St. Louis et al., 1994), managers can use the results of this study to more accurately weigh the benefits and risks associated with proposals for constructed wetlands within the watershed to reduce phosphorus loading to the James River (WWEI, 2002). The results of this study should also prove helpful to community and state officials who have sought in vain to explain periodic mercury concentrations in stream water within the watershed (Barnes, 1995). Finally, plans to redevelop the Jordan Creek valley may incorporate the results of this study in making an increased effort reduce sediment lost to the stream during construction phases.

The geochemical sediment quality assessment of Wilson Creek watershed will provide spatial and temporal information about mercury sources, substrate associations, storage, and sedimentation characteristics within the watershed. Elevated levels of mercury in active channel sediment will illuminate non-point sources within the upper watershed and recent sources in the lower. Geochemical substrate associations unique to the lower watershed will help identify mercury source locations. Historically-contaminated sediment in the overbank environment will be evaluated as a recent source of mercury to the stream. This thesis shows that there are differences in mercury storage magnitude between the upper and lower watershed and that different mercury transport processes are at work within these stream reaches. Stored mercury in the alluvial deposits of the Wilson Creek watershed may serve as a contaminant source to downstream receiving waters for years to come.

CHAPTER TWO:

LITERATURE REVIEW

The spatial and temporal distribution of contaminated sediment within the channel and overbank environments in Wilson Creek can generally be described as the product of a few factors: the location and magnitude of pollutant sources within the watershed, the physical and chemical characteristics of the sediments, and the fluvial transport processes at work over time (Phillips, 1988; Pavlowsky, 1995). The pollutant sources in the watershed were described in the previous chapter, leaving sediment-pollutant associations and pollutant-bound sediment transport literature to be explored in this one. While the primary focus of this study is the distribution of mercury from urban sources in channel and overbank sediment at the watershed scale, the paucity of studies in this specific area will require this review to expand into the examination of mining-related trace element literature as well as studies dealing with the distribution of mercury in urban streams.

SEDIMENT ASSOCIATED TRACE ELEMENTS

The bottom sediment of aquatic environments are natural sinks for nearly all EPA trace element priority pollutants (Horowitz, 1991). The elements: Arsenic (As), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Selenium (Se), Silver (Ag), Thallium (Tl), and Zinc (Zn) have low solubilities and can be removed from solution, or from a free ionic state, by chelation, precipitation, and predominantly by adsorption (Forstner and Wittmann, 1981; Yong et al., 1992). Adsorption takes place at the sediment–water interface due to intermolecular forces electrostatically attracting positively charged pollutants (cations) to negatively charged fine-grain particles (anions). Concentrations of trace elements are found to be up to

100,000 times higher in bottom and suspended sediment than in solution with solubility increasing in acidic waters as positively charged hydrogen ions compete with cations for adsorption sites (Forstner and Wittmann, 1981).

Due to its low solubility, concentrations in stream water remain relatively low causing mercury to accumulate in bottom sediment in mostly inorganic (> 98 %) forms (Faure, 1991). Thus situated, mercury can undergo bacteria-mediated conversion to the more bioavailable and toxic organic species like methylmercury which account for over 80 % of mercury in fish (Forstner and Wittmann, 1981; Fergusson, 1990; Goldman and Shannon, 2001; Gray, 2003). Bioaccumulation of mercury in humans and piscivorous wildlife can reach dangerous levels in susceptible populations causing impaired development and death (USEPA, 2000). This potential was demonstrated in the U. S. when high mercury levels in fish were detected in the St. Clair River – Lake Erie system in the early 1970's (Bails, 1972). Concentrations of mercury in water samples were very low while bottom sediment levels were high, indicating the role of sediments as a major mercury sink within the stream system.

DOWNSTREAM DISTRIBUTION TRENDS

Streams are dynamic entities that not only complete the hydrologic cycle by returning water to the oceans, but also modify the basins in which they flow by means of the fluvial processes of erosion, transportation, and deposition of sediment. A basin's hydrologic characteristics and the quantity and type of sediment at any one location along its channel are dependent upon upstream climate, geology, physiography, and human activity (Knighton, 1998). The concentrations of sediment-bound metals within longitudinal

deposits are also dependent upon these factors and have long been known to exhibit an inverse exponential relationship with increasing distance downstream from the source (Wertz, 1949). This relationship, termed the “longitudinal decay” or “negative exponential” model, can be caused by many factors including adsorption and storage, changes in form or solubility, biotic uptake, and dilution by tributaries, and it has long been utilized for mineral reconnaissance and more recently for pollution assessments (Rose, 1970; Hawkes, 1976; Phillips, 1988). The investigations discussed here provide background information necessary to understand metal distribution in active channel sediments and describe the factors that tend to influence concentration variability, methods of sample collection and analysis, and geochemical source identification.

Rose et al. (1970) describes the use of multiple regression techniques to explain the downstream variation in concentration of ore indicating metals such as zinc and copper. Predictor variables expected to account for drainage area dependent concentration variability were upstream lithology, relief, and metal-rich fines in the sample as indicated by iron, manganese, clay-sized particle, and organic matter contents. Step-wise multiple regression indicated that lithology, relief, and iron and manganese oxides were significant variables in their effect upon downstream concentration. Through this technique they were also able to select a value to separate anomalous (ore indicating) concentrations from background (noise) values. They also suggest that aluminum could be successfully used as an index of clay content and, in some areas, silicon for metal-poor quartz content.

Hawkes (1976) developed an idealized dilution formula for selecting sample site locations and interpreting metal concentrations in mining reconnaissance surveys. Using sediment concentrations and upstream drainage area at sample sites, determinations of ore

grade and / or extent of upstream mineralized zones could be made. Although the model assumptions of uniform erosion, single source, no sampling error, and no sediment-water metal exchange may not be applicable to the complex pollution characteristics of an urban area, the validation of his formula in identifying copper deposits is evidence that definable downstream distance dilution relationships can be developed and employed to account for metal distribution patterns in stream sediment. Goodyear et al., (1996) confirmed the weakness of Hawkes' idealized model in predicting downstream dispersion of lead and zinc from anthropogenic sources.

Phillips (1988) used the spatial concepts developed by Rose and Hawkes to develop a probabilistic model to assess the risk of copper contamination in stream water. The simplicity of this approach relies upon the assumptions that the pollution load at the mouth of the stream is a function of two basic factors: (1) the magnitude of non-point source pollutant contribution from the site to the stream (loading), and (2) the downstream transport distance. This distance decay function rests on the assumption that "pollutants will decay, change forms, be incorporated by vegetation or other matter, become adsorbed onto sediment, or be deposited and stored for variable lengths of time." Phillips' study demonstrated that the application of spatial concepts to stream sediment metal data will aid resource managers in the spatial allocation of resources to the most severely affected areas or to the areas where the most beneficial results can be achieved.

CHANNEL MERCURY DISTRIBUTION

Urban Industrial Sources

Waslenchuk (1975) investigated mercury in channel sediments within a 6 km reach of the Ottawa River at Ottawa. This reach contained elevated levels of mercury due to pre-1971 discharge of effluent from a pulp mill. He noted that mercury found in suspended sediment was complexed with organic acids and colloidal-clay sized particles. He points to the low biomass in the stream as the reason that little methylation of mercury occurred. Waslenchuk observed that, without additional mercury input, concentrations in channel sediments at a particular site would decrease over time by either mechanical or chemical processes. The mechanical processes of stream flow promote dilution and mixing as clean sediment is introduced to a stream reach and some contaminated sediment is lost downstream. The chemical processes at work in the Ottawa River involved desorption and dissolution whereby mercury is liberated from its association with the aging ferric hydroxide coating of grain particles. This liberated mercury can associate with fresh ferric hydroxide or be released down stream in solution. He estimated the exponential decrease of mercury to be 50% annually or having a half-life of 0.78 to 1.15 years. Waslenchuk pointed out that although these processes represented a "recovery" for the channel sediment of the study area, the mercury was not removed from the system. Desorption and dissolution processes in Wilson Creek may be especially important in mobilizing mercury to the water column at locations where water chemistry changes, such as locations below the Southwest WWTP.

Heaven et al. (2000) measured mercury in the bed, bank, and floodplain sediments of the River Nura, Kasakstan, for 70 km downstream of an acetaldehyde plant. Mercury wastes were dumped into the stream and adsorbed to large volumes of silt-sized power station fly ash that was subsequently transported and distributed downstream. Average concentrations in bank sediments were 73.3 ppm near the plant and decreased to 13.4 ppm at 70 km downstream. Highest concentrations were observed in the bed sediment within the first 25 km downstream of the plant and in the bank and floodplain deposits thereafter. These findings suggest that large amounts of mercury were transported away from the source and deposited on downstream banks and floodplains. High bed sediment mercury concentrations in the upstream reaches suggest that contaminated sediment is still being transported from the sources near the plant.

Van Loon (1974) measured sediment mercury levels using flameless AAS above, near (0-100 m), and below (1000 m) waste water treatment plant (WWTP) outflows in four streams in Canada. Mercury concentrations within 100 meters downstream of the outflow increased nearly two orders of magnitude over upstream concentrations and quickly attenuated downstream approaching above outflow concentrations within 1 km in most cases. Comparative water samples suggested that most mercury transport occurred in particulate phase being readily incorporated in the bottom sediment. High mercury levels were also measured in fertilizers (0.4 – 10 ppm) and waste sludges (1 – 25 ppm) used as fertilizer for residential gardens and agricultural fields. Municipal WWTP's spatially concentrate mercury from diverse sources, perhaps even outside of the watershed, and deliver it to aquatic environments via direct discharge to the water column

and at diffuse non-point sources where the contaminated sediment of sludged soils are eroded and washed into streams.

Birkett (2001) evaluated the distribution of mercury in channel sediments within the River Yare in Norfolk, UK. A waste water treatment plant discharged treated effluent to the river from many generation sites within the Yare catchment. One such site was a chemical / pharmaceutical company that was known to dispose of waste water containing mercuric chloride, mercurous chloride, and mercuric iodide between 1964 and 1986. Starting at 3.35 km upstream of the treatment plant, five equally spaced grab samples were collected across the width of the stream at nearly each of 38 transects at 1 km intervals following the river's course until it empties into Breydon Waters near the North Sea. Cold vapor flow injection atomic absorption spectrophotometry (CV-FIAAS) was used to determine total mercury. Birkett observed the distance decay trend, describing it as a “distinct pollution plume” characterized by increasing concentrations for the first few kilometers reaching peak concentrations of 6600 ppb at five km downstream of the source followed by downstream attenuation. Peak concentrations are nearly 20 times higher than accepted regional background levels of 390 ppb (Downs et. al., 1999). This study points out that channel morphology and mercury associations with finer grain particles and organic matter was found to play an important role in the location of peak mercury concentrations within transects. Significantly higher mercury concentrations were found in sediments on the inside bends of the river where velocities are lowest, resulting in the accumulation of finer grain sediment, and where organic matter was present. Table 1 below is modified from Birkett's. Notice the drastic contrast between studies examining mining sites (bottom third) and those investigating non-mining sites.

Table 1. Downstream distribution of mercury (Hg) in Channel sediment.

Stream	Hg Source	Analysis	Bkgd*	Maximum*	Near Source*	Downstream*	Reference
Don River, Canada	WWTP	Fl AAS	50 ^a	N.D.	3,800 (0.1)	60 (1)	Van Loon (1974)
Don River, Canada	WWTP	Fl AAS	60 ^a	N.D.	1,200 (0.1)	120 (1)	
Credit River, Canada	WWTP	Fl AAS	250 ^a	N.D.	3,800 (0.1)	110 (1)	
Humber River, Canada	WWTP	Fl AAS	150 ^a	N.D.	900 (0.1)	500 (1)	
River Yare, UK	WWTP	CV-FIAAS	400	6,600	6,600 (5)	150 (10)	Birkett (2001)
River Nura, Kasakstan	Indus. Waste	NS	NS	100,000	73,300	13,400 (70)	Heaven et. Al (2000)
Fields Brook, Ohio	Indus. Waste	Au Film	24	20,600	20,600	119 ^b	Anderson & Carlson (1987)
Wilson Ck. (Upper), Missouri	Hist. Indus.	CVAAS	20	1,240	720 (0 ^c)	160 (5.5)	This Study
Wilson Ck. (Lower), Missouri	Unknown	CVAAS	20	1,940	700 (1 ^c)	173 (9)	
Quantico Ck., Virginia	Hg Mine	NS	NS	3,670	3,670 (0)	90 (11)	Seal (2002)
Vadleazogues R., Spain	Hg Mine	CVAAS	550	1,005,000	60,000 (0 ^c)	107,000 (45 ^c)	Nevado et al. (2002)
Tagbueros Ck., Philippines	Hg Mine	CVAAS / AFS	100	15,000	9,400 (0)	7100 (3)	Gray et al. (2003)
Eldorado Creek, Nevada	Hg Mine	CVAAS / AFS	440	170,000	1,700 (0.1)	870 (2)	Gray (2003)
Clear Creek, Nevada	Hg Mine	CVAAS / AFS	440	170,000	2,600 (0.3)	240 (4)	
Spring Creek, Nevada	Hg Mine	CVAAS / AFS	440	170,000	60,000 (0.4)	230 (8)	

*Mercury concentration in ppb (km downstream from Hg source)

^a Above outfall

^b In Ashtabula River immediately downstream of Fields Brook confluence

^c Hg sources located along entire stream reach

Bkgd – regional background mercury levels

NS – not specified

WWTP – waste water treatment plant

AAS - atomic absorption spectrophotometry

Fl AAS flameless atomic absorption spectrophotometry

CVAAS - cold vapor atomic absorption spectrophotometry

AFS - cold vapor atomic fluorescence spectrometry

CVFIAAS - cold vapor flow injection atomic absorption spectrophotometry

Mining Sources

Nevado et. al. (2002) have documented the concentrations of mercury near Almaden, Spain, home to the world's largest mercury mine still in operation, by testing water, sediment, and biota within the Vadleazogues River, from its headwaters to its terminus at the La Serena dam. Channel samples of less than 5 cm depth were collected in polyethylene bags at 9 sites, passed through a 2 mm sieve, ground in an agate mortar to a 63 um particle size, and tested for mercury using cold vapor atomic absorption spectrometry (CVAAS). Nevado points out readings for carbon as less than 2% for all samples as indicating the non-organic character of the sediments. Background levels of 0.53 ppm and 0.57 ppm were determined by testing two sites outside areas of direct mine tailings deposits and were one order of magnitude higher than regionally normal concentrations reported by Andersson (1979). Channel sediment concentrations ranged from 6 to 107 ppm for most sites with one site testing at 1005 ppm. The mercury in water samples was also high at this site (20 ug/l) while nearly all others were below detection limits of 0.11 ug/l. For comparison, The Environmental Protection Agency (EPA) has set recommended maximum in stream concentrations at 2.4 ug/l (EPA, 1992) and the European Union's average monthly maximum concentration is set at 1.0 ug/l for surface waters. Mercury in the bivalves tested ranged from 1.57 to 4.10 ug/g with the average just over the 0.5 ug/g level permissible for consumption by the World Health Organization (WHO-IPCS, 1990). A very interesting finding of this study is that although organic mercury compounds were not detected in the sediments, 17 % to 40 % of mercury found in the bivalves was methylated. This high sediment to tissue

accumulation factor may indicate that measures of inorganic mercury in the sediment "are almost certainly a continuing source of mercury to organisms.

Gray et al. (2003) measured mercury levels in mine-waste calcine piles, water, lake sediment and stream sediment near the Palawan Quicksilver mine in the Philippines. Concentrations in all but one Tagbueros Creek sediment samples near and downstream of the mine (3.7 – 15 ppm) were elevated over the upstream site (4.2 ppm). However, not enough samples were collected to observe any distance trend. Mercury concentrations in water samples draining calcine piles and mine waters were high and acidic (pH 3.1 – 4.3) suggesting high mercury solubility at low pH values.

Gray (2003) measured elevated mercury concentrations in the sediment of streams located in close proximity to abandoned mercury mines in the Humboldt River basin. The downstream mercury trend displayed rapid dilution from maximum concentrations of 170 ppm to near region background levels of 0.44 ppm within 5 to 10 km downstream of the mines. Dilution was attributed to inputs of unmineralized detritus. Mines located away from streams (> 8 km) had little effect on mercury concentrations in the stream sediment even though calcine material concentrations were very high (up to 1300 ppm). Mercury concentrations in ore were as high as 6.9% in the region.

Gray (2000) measured total mercury, methylmercury, and mercuric ion in water, sediment, and fish in streams draining abandoned mercury mines in south-western Alaska. Mercury concentrations in stream sediment samples were as high as 5,500 ppm at sites near the mines. Mercuric ion concentrations (< 5 %) and methylmercury concentrations (< 1 %) were a small fraction of total mercury in stream sediment.

Fang et al. (2004) found measured (gold film Hg detection) mercury concentrations in stream sediment to be a useful pathfinder in mapping the borders of known gold deposits. Sediment concentrations ranged between 18 and 2,000 ppb with all values over 350 ppb found within 2 km of gold-bearing veins. The authors suggest 1 km sample intervals for future reconnaissance of targeted areas. Gold film detection method was cheap and could be done in the field with electricity and adequate ventilation.

Domagalski (1998) measured total CVAAS mercury and methylmercury in bed sediment (17 sites) and water (12 sites) of streams within the Sacramento River Basin. Mercury mining in the Coast Ranges of the northern basin and gold mines in the Sierra Nevada to the east were known sources of mercury to streams. Bed sediment mercury was elevated above average crustal mercury abundance (50 ppb) and ranged from 10 ppb to 370 ppb having a mean of 280 ppb. The highest mercury levels in bed sediment were found in streams draining the Sierra Nevada. Reservoirs were determined to be a significant sink for sediment-bound mercury. A region producing the greatest increase in mercury loading, as measured by water samples during a winter flood event, was clearly identifiable as a possible source region in the bed sediment trend. This study emphasizes the importance of bed sediment sampling as a means of capturing a time averaged representation of overall mercury trends without the logistical problems and financial burden of water sampling during flood events.

Seal (2002) measured mercury in soils, stream sediment, water, and biota below the abandoned Greenwood gold mine in northern Virginia. Concentrations decreased from 3.67 ppm at the mine to 0.09 ppm 11 km downstream. On a much larger scale, Lechler et al. (2000) determined that elevated mercury levels in water, sediment, soils, and fish

along a 900 km reach of the Madeira River in Brazil was due primarily to natural sources and biogeochemical processes and not from upstream gold mining using mercury amalgamation which had only localized effects.

Graf (1985) examined the sediment- mercury loading to Lake Powell from its 279,000 km² basin area within the Colorado Plateau. Sediment mercury concentrations were measured by using AAS in the < 0.2 mm fraction. Mercury concentrations in channel sediment did not generally decline in the downstream direction because the primary mercury inputs were not discrete point sources, but the geologic units through which the stream flowed. Graf determined that mercury contribution to the lake was dependant upon sediment yield and source area lithology and not upon proportion of water contribution. He concluded that mercury accumulation in the sediment of contributing streams was not strongly related to particle size or organic matter content. Mercury concentrations in stream sediments were generally not enriched over mercury levels in the host rock as is usually the case in humid areas. Graf concluded that spatial patterns are at least as important in mercury loading to Lake Powell as chemical considerations (e.g. differences in mercury contribution from tributaries are linked to sediment contribution, which in turn, is linked to geomorphic processes).

Controls by Fluvial Processes

The decay of pollutant concentrations with increasing distance downstream from the source is influenced not only by chemical factors but also by geomorphic considerations. The following two studies are briefly discussed to clarify some of the pollutant concentration controls exerted by fluvial processes. Graf (1990) examined the downstream distribution of thorium-230 in the Puerco River, New Mexico, after the dam

failure of a uranium tailings pond. Downstream distribution did not match the typical attenuation patterns typically expected. Distribution was instead influenced more by hydraulic and geomorphic considerations resulting in inverse variations in thorium concentrations and stream power due to changes in lithology and cross-sectional channel area.

Graf (1996) suggest that distance decay functions may only be observed at small scales within a basin. He describes the stream system as being complex and divided into several segments with internal processes that differ from those of neighboring segments.

Differentiating these segments and determining the important physical processes within each is the key to understanding the distribution of sediment-bound pollutants at the watershed scale. Graf suggests five characteristics of fluvial systems that act to complicate a smooth decay with increasing distance:

- 1) hydraulic processes sort sediments, transporting fine particles greater distances.
- 2) Wave movement of sediment through system instead of consistent and constant transport (e.g. more sediment transport during the rising limb of the hydrograph).
- 3) Sediment can be stored within the system and be remobilized thus acting as an additional source.
- 4) Deposition occurs where stream power declines. This is due to “geomorphic factors” that may not be stream related. Graf gives two examples: change in geologic substrate and colluvial processes adjacent to the channel (e.g. debris from canyon walls restricting the channel). For Wilson Creek, such factors may include: karst features such as swallow holes or losing sections and springs; Urban

development such as bridge construction, bank stabilization, fences causing debris dam, WWTP outflow, storm drains, and cattle access.

- 5) Tributary streams introduce sediment of varying contamination levels and change the amount of sediment stored and transported, diluting or increasing the concentration of sediment-bound pollutants.

Graf (1996) writes that the geographic variation in the primary transport controls (stream power and hydraulic resistance) is responsible for the distribution of pollutants in a manner that deviates from a smooth distance decay model. Stream power and resistance together produce the geomorphic work of storing and transporting contaminated sediment. Because the spatial variability of these controls can be investigated and predicted, the subsequent transport and storage of contaminated sediment can be understood and its “distinctive and predictable geography” described.

OVERBANK POLLUTANT DISTRIBUTION

The studies discussed above provide clear precedent for using channel sediment to assess the movement of mercury through the stream. However, analysis of sediment stored in the floodplain can provide information on past pollution events. This is important because it is becoming increasingly evident that much of the pollution signal detected within channel sediment is not the result of recent releases, but the reintroduction of floodplain sediment. With this in mind, knowledge of pollutant distribution within the entire stream system will be essential to understand how to manage and regulate the level of pollutants in the aquatic environment. The studies reviewed here provide information on sampling methods, the influence of human activity

on sedimentation rates, historic and pre-history deposition, interpreting background concentrations, and determining the timing of pollutant releases from the sediment profiles. For discussion here, overbank deposits refer to the alluvial deposits within the floodplain and low terrace adjacent to the channel.

Knox (1987) investigated floodplain development and sedimentation rates of the upper Mississippi valley in the Driftless area of southwestern Wisconsin. He used pre-settlement soils and the timing of known trace element contamination to date the alluvial sediments of the area. Happ, Rittenhouse, and Dobson (1940) were cited as having shown that early agricultural practices were the cause of most of the overbank sedimentation that covered the dark mollisol that dominated the region before white settlement. Thus the presence of the buried mollisol was an indicator of the pre-settlement floodplain. Lead and zinc mining were also prevalent in the area with lead production peaking between 1845 and 1847 and zinc production experiencing two peaks in 1906-1910 and the late 1940's - early 1950's. Knox points to the work of Macklin (1985) who determined that in fine grained sediment the concentrations of heavy metals stay relatively stable in the stratigraphic profile. Variations in the concentrations of these metals within the overbank profile were used to indicate age and relative rate of deposition. Knox concluded of three variables (landuse, climate, and channel morphology) that influenced accelerated floodplain deposition, landuse changes represented the most important factor in the study area.

Leigh (1995) examined the effects of gold mining on the floodplains of Yahoola Creek and Chestatee River within the Dahlonega Gold Belt of northern Georgia. Mercury was used to amalgamate gold in the extraction process and was subsequently released to the

streams as waste. Leigh focused on the distribution of mercury and increased sedimentation from hydraulic mining practices to date downstream overbank sediment profiles. A primary objective was to identify pre and post 1829 (gold rush) floodplain sediment. Sediment samples were collected in 25 cm units to 3-4 m depths at fresh cutbanks every 2-4 km along the two streams. Samples were tested for particle size by a modified pipette and sieve method (Indorante et. al., 1990), organic carbon by wet oxidation using the Walkley-Black method (Janitsky, 1986), and mercury in the less than 0.177 mm fraction by vapor release upon heating with vapor phase atomic absorption and in the total sample by CVAAS. Leigh determined average background mercury to be 0.04 ppm which was close to those found in crustal rocks of the area 0.05 ppm (Baudo and Muntau, 1990) and soils 0.07 ppm (Adriano, 1986). He found that mercury concentrations in the floodplain sediment ranged from 0.04 ppm to 3.9 ppm, decreased with increasing distance from the source area, and fell below 0.1 ppm within 10 to 15 km down stream. He cites Giesy and Hoke (1990) and Ginn and Pastorok (1992) for sediment standards of 0.1 to 1.0 ppm, which were exceeded by several of his sample sites. Channel sediment samples were all low in mercury (< 0.1 ppm) except one collected near the “heart of the mining district.” Buried soils were observed at some sites and confirmed by organic matter spikes at corresponding depths. Leigh found relatively high sedimentation rates of 1-3 cm / year during the years of erosive mining activities and that modern storm events rarely overflow the banks due to extreme down cutting as the streams adjusted to new equilibrium conditions in the post mining watershed.

Leece and Pavlowsky (1997) sampled overbank, point bar, and channel deposits within the main stem and tributaries of the Blue River. This river drains a portion of the

lead and zinc district described above in the discussion of Knox (1987). This study investigates the spatial distribution of zinc within the floodplain, considers the function of floodplains as a semi-permanent sinks for metal contaminants, and evaluates reaches of the stream for their potential to release stored pollutants from the floodplain due to lateral migration. Cross sectional areas were used to calculate the mass of floodplain sediment with zinc concentrations within the mined watershed estimated using regression equations. This information, combined with known or predicted areas of lateral stream migration, predicted locations where remobilization of contaminated sediment was most likely to occur. With five times more zinc found in overbank deposits in comparison to pointbar deposits, this study demonstrates the importance of considering the floodplain as a temporary sink for pollutants.

Lecce and Pavlowsky (2001) later examined the spatial and temporal variations in sedimentation rates within the Blue River watershed using mining-related zinc concentrations in overbank sediment. Their results suggested that floodplain topography affected sedimentation rates with lower floodplain surfaces having higher rates of sedimentation. In addition, channel enlargement in the upper watershed tended to increase lower watershed sedimentation rates. Finally, the results of Lecce and Pavlowsky's (1997, 2001) studies are congruent with those of Graf (1990, 1996) described earlier which emphasize that in order to fully evaluate the long-term contaminant distribution within a watershed, geomorphic and sediment transport processes must be considered instead of relying only on distance decay functions.

TRACE ELEMENT STUDIES IN SOUTHWEST MISSOURI

It is clear that the analyses of channel and floodplain sediments are useful in examining the spatial and temporal distribution of mercury and other trace elements in the stream environment. Although no watershed scale studies of mercury in fluvial sediments have been found for the southwest Missouri area, a few investigations of other trace elements are discussed here.

Gutierrez et al. (2004) measured the concentration of trace metals, arsenic and selected geochemical substrate indicators in water and also in the stream sediment of caves in southwest Missouri using sequential extraction. The sampling site affected by urban groundwater recharge had elevated metal and arsenic concentrations similar to those found in a nearby stream. This suggests that the urban pollution signal experienced very little attenuation from the watershed surface to stream channel sediment deposits via groundwater transport. Trace metal transport through karst solution conduits may substantially affect stream sediment pollution trends in areas of the Wilson Creek watershed with developed karst terrain and complex hydrology.

Mantei and Foster (1991) tested channel sediment in the South Dry Sac and Little Dry Sac Rivers just north of Springfield. Samples were wet sieved at the collection site with the very fine sand fraction ($>0.074\text{mm}$ to $<0.88\text{mm}$) saved for analysis. This was done to capture a grain size fine enough to accumulate high concentrations of metals yet large enough to limit transport and thereby lengthen residence time at one location. Geochemical phases of exchangeable cations, carbonates, manganese oxides / hydrous oxides, iron oxides/hydrous oxides, organics, and remnant classifications were examined.

With the exception of cobalt, manganese, and barium all other elements tested (mercury excluded) had high affinities for iron and remnant phases.

Mantei and Sappington (1994) tested for trace elements within the channel sediments of three rivers near a landfill in Wright County. Particle sizes less than 0.0625 mm and between 0.149 mm and 0.25 mm were dry sieved and saved for analysis. This study failed to detect a decrease in metal concentrations in a down stream direction as was expected. This could be due, however, to the very small size of the study reach (~6 km). The study concludes that metal enrichment was greater in the finer particle size samples and that sediment analysis studies would be helpful in directing bio-monitoring studies to areas of possible ecosystem impact.

Both of the studies discussed above used AAS to determine trace element concentrations. Maximum concentrations were detected at the landfill sites and downstream of the waste water treatment facility. These findings lead the authors to conclude that stream sediments are an effective means of identifying emission sources of trace elements.

Sutton (1981) examined landfills as non-point pollution sources near streams in Springfield. She reasoned that the leaching of trace elements from landfill waste would flow through the area's porous limestone and contaminate ground and stream water. Sutton collected 35 - 40 soil samples from each of four abandoned landfills located in the floodplains of the Little Sac River, Wilson Creek, and Jordan Creek (within the Wilson Creek watershed). Soil samples were ground by pestle and mortar, sieved, and analyzed for cadmium, chromium, copper, nickel, and lead by atomic absorption spectrophotometry. The results revealed anomalous values for each metal for both

landfills within the Wilson Creek watershed. The Jordan Creek landfill had been abandoned for the longest time and its soils measured the highest concentrations. Bennett Street landfill, the next oldest, had the second highest concentrations. Sutton concluded that contaminant dispersion increased over time and that soils over, and presumably beneath, the landfills pose a risk to surface and ground water in the region. Sutton suggests monitoring and tracing to detect the movement of these metals toward adjacent streams.

Pierce (1992) tested for the trace elements of barium, calcium, cobalt, chromium, copper, cadmium, iron, manganese, nickel, lead, silver, and zinc in the channel sediments of Wilson Creek. He investigated the impact of effluent from the Southwest Waste Water Treatment Plant on heavy metal content in the stream and designed his study to detect its influence. Sixteen samples were collected at one eighth mile intervals upstream and downstream of the treatment plant and one at the plant's outflow. Samples were sieved and the 140 - 200 mesh size particles were analyzed using AAS. A two sample t-test revealed significant increases for silver, chromium, copper, manganese, cobalt, and barium in downstream sediments. However, concentrations began to increase upstream of the plant's effluent. Pierce reasoned that the year round flow regime established by the introduction of plant effluent to the otherwise intermittent stream would allow for the concentration of trace metals in downstream sediment to be higher than those upstream. He emphasizes that the plant effluent is not responsible for the increase since concentration increase initiated upstream and are more likely due to industries in west Springfield. Pierce recommended future testing of the entire creek and its tributaries incorporating other aspects of the stream environment.

SUMMARY

The reviewed stream sediment mercury and trace element studies have demonstrated that downstream attenuation in mercury concentration below source regions are common, that geomorphic processes and chemical considerations are important in mercury dispersal patterns, and that stream sediment assessments can accurately measure mercury trends and identify source regions at watershed-scale. Variable downstream mercury dispersal in channel and overbank sediment deposits below sources was observed with peak levels between 0 and 5 km and attenuation to background levels between 1 and 15 km. Both point and nonpoint sources patterns can be associated with WWTP's. Geomorphic factors such as grain-size sorting, overbank deposition, sediment availability, and dilution can be as important as the chemical considerations of adsorption and release from geochemical substrates.

The reviewed studies also brought to light factors important to the investigation of mercury trends in the stream sediments of Wilson Creek and sampling and analysis procedures that need to be considered. Channel geometry alterations due to urbanization, the contamination level of overbank deposits, sediment and water inputs from tributary streams, the location WWTP outflows and closed landfills, and karst terrain features may affect sediment mercury distribution within the Wilson Creek watershed. Samples should be collected from both the active channel and overbank sediment deposit environments to provide information on recent and historical pollution trends. Only sediment less than coarse sand (2 mm) should be retained for geochemical analysis. Finally, geochemical information regarding both pollutant and substrate indicating elements should be obtained in order to adequately describe mercury distribution trends.

CHAPTER THREE:

DESCRIPTION OF STUDY AREA

This chapter provides the geographic context within which the research problem, investigative methods, and analytical results can be understood and applied. It focuses upon the physical description of the Wilson Creek watershed within the Ozark physiographic region. In addition, pre-settlement through modern-day land use and land cover characteristics are briefly described as a determining factor in the sediment-contaminant transport and storage processes operating within the watershed.

REGIONAL SETTING

The Ozark physiographic province lies mostly within southern Missouri and is nestled between the Atlantic and Interior Plains divisions of North America (Fenneman, 1946) (Figure 1). The Wilson Creek watershed consists of 218 km² of southern Greene and northwestern Christian counties of Missouri within the James River Basin (Figure 2). The Wilson Creek watershed receives surface runoff from the city of Springfield, the largest urban center in the Ozarks and the third largest in the state, and from residential and agricultural properties southwest of the metropolitan area (Figure 3). The water and sediment of Wilson Creek flow into the James River, which empties into the White River system at Table Rock Lake. Previous bottom sediment sampling indicates that most sediment-bound pollutants from the James River are deposits within the James River Arm of Table Rock Lake (Owen, 2003). The White River joins the Mississippi River in Southeastern Arkansas.

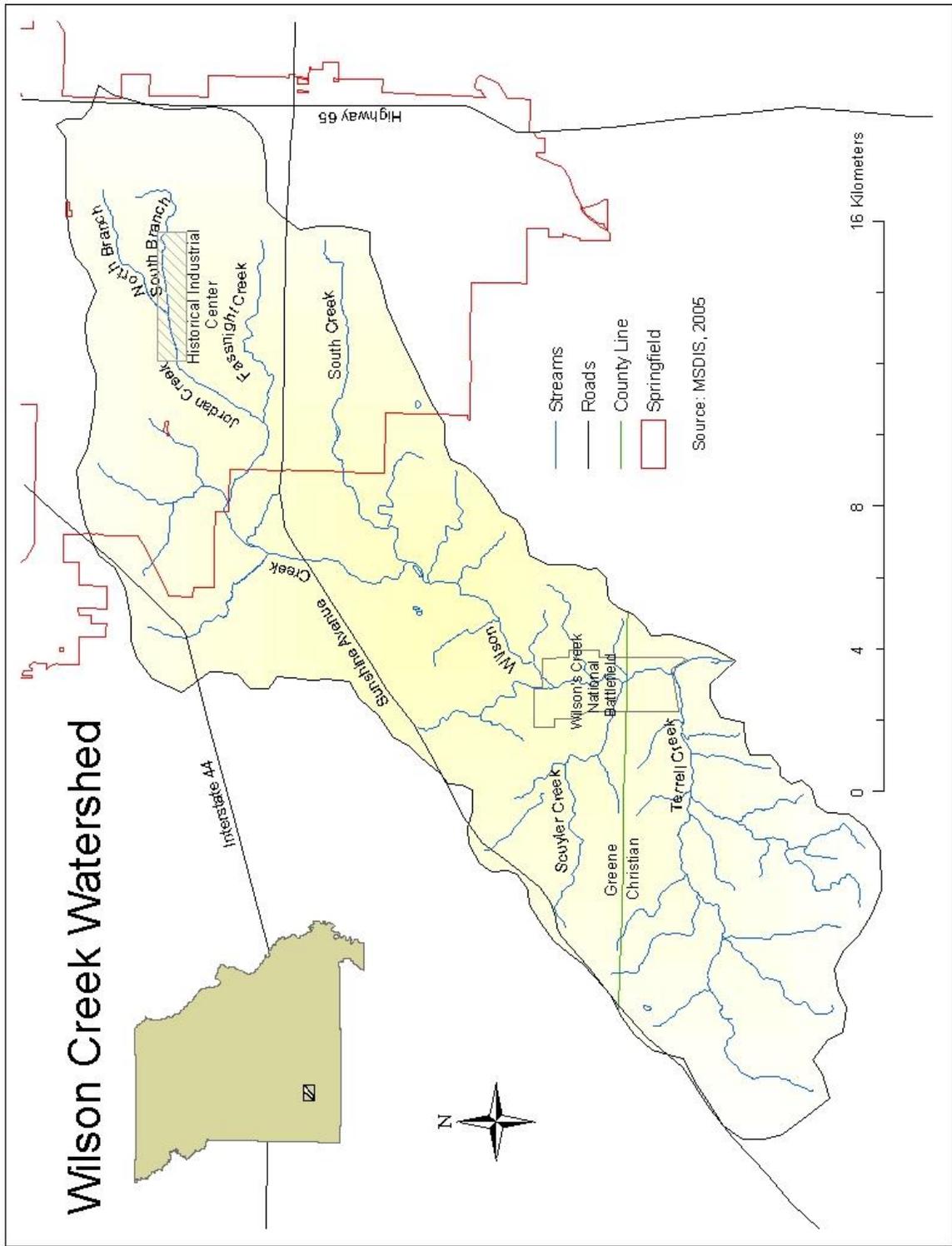


Figure 3. Wilson Creek watershed.

GEOLOGY

The bedrock underlying the Wilson Creek watershed primarily consists of several layers of Mississippian age limestone (Figure 4). Relatively small outcrops can be observed throughout the watershed's surface and are especially common within the stream channel where erosion has removed soils, residuum, colluvium, and alluvium layers (Figure 5). Six different light to medium grey to brown colored limestone formations are exposed within the watershed as the channel has down-cut through these uplifted horizontal layers of carbonate rock. The mineral composition and trace element content of stream sediment within the watershed should not display any spatial patterns owing to distribution of these similar bedrock units. These formations can be seen grouped into three mapping units in Figure 4: the Mississippian Osagean (Mo) series, with Keokuk and Burlington Limestones, Pierson Limestones, and Elsey and Reeds Spring Formations, occurs throughout the watershed while the Mississippian Meramecian (Mm) series (Warsaw Formation) and Pennsylvanian Channel Sandstones (Pcs) are found only in small isolated areas (Middendorf et al. 1991). The Lower Mississippian Keokuk and Burlington limestones are of coarse to fine crystalline texture, have abundant bands of chert, have a highly irregular surface due to solution, and have a maximum thickness of 61 m. The Short Creek Oolitic limestone rests atop of the Keokuk in some location in a 0.6 - 2.4 m layer.

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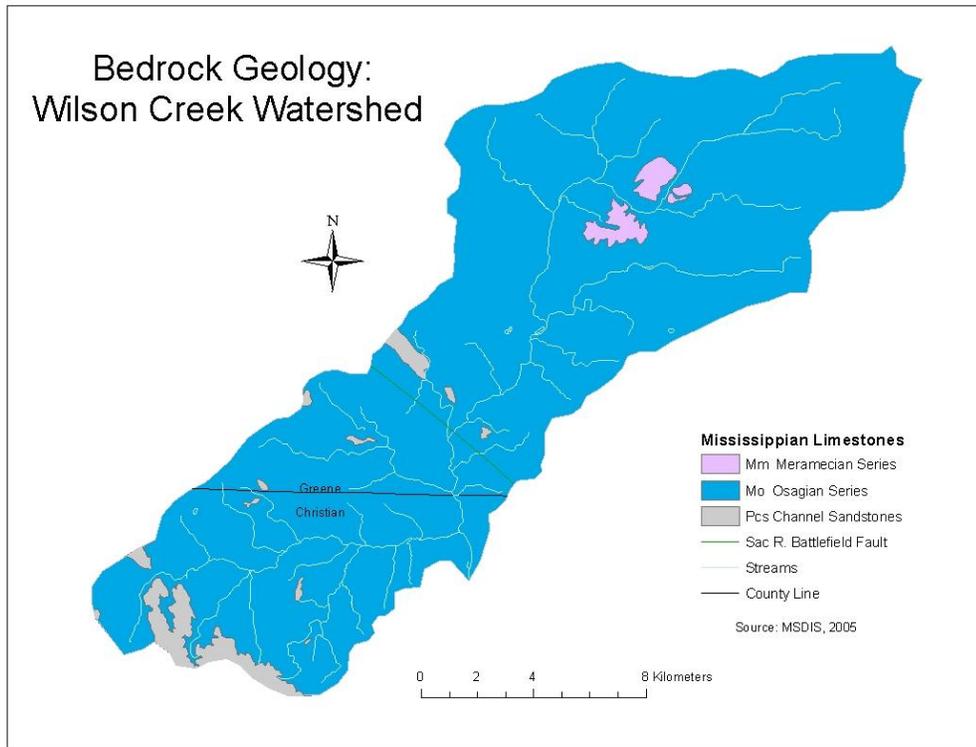


Figure 4. Bedrock Geology of the Wilson Creek watershed.

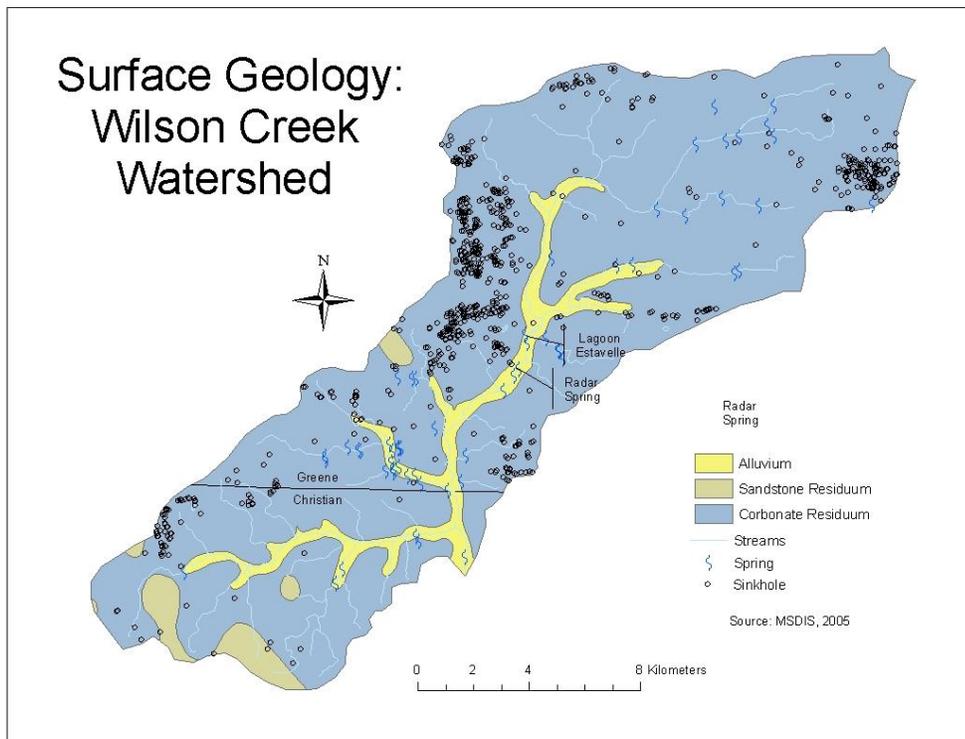


Figure 5. Surface Geology and karst features of the Wilson Creek watershed.

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The fine grained Elsey formation has a maximum thickness of 24 m and contains white to grey nodular chert and elongated chert lenses of a mottled brown color. In some locations, chert may constitute up to 60% of the formation's volume. The 15 m thick Reeds Spring Formation has a fine crystalline texture, is grey to brown in color, and contains up to 40% of blue, brown, and dark grey chert. The Pierson limestone has a medium grained texture and is brown to tan in color. The relatively young Upper Mississippian Warsaw Formation consists of coarse to medium crystalline texture crinoidal limestone, commonly has white chert nodules, and extends to a maximum depth of approximately 24.4 m (Middendorf et al. 1991).

Two known faults extend across the watershed within these upper sedimentary rock layers. Fassnight Fault, which is approximately 10 km long, parallels Fassnight Creek for a short distance in a northwest to southeast direction across Springfield. The 45 km long Sac River / Battlefield Fault (Figure 5) trends in a northwest to southeast direction from south of Ash Grove, Missouri to the Finely Creek just south of Nixa, Missouri. This fault crosses the Wilson Creek at the northern boundary of the National Park.

KARST

Naturally acidic rainfall infiltrating along the fractures and bedding planes of the carbonate rocks described above, especially the thick Burlington – Keokuk formations, have created above and below ground drainage networks by solution of the calcium carbonate rich limestone. In some areas, the solution of bedrock material is often the predominant erosional agent and the geologic features that develop under such circumstances are termed karst.

Karst features can be grouped into one of four general categories: (1) recharge features such as sinkholes, losing streams, and swallets where surface water can enter underground passages on the land surface or within a streams channel; (2) transport features such as caves and conduits where water is, or once was conveyed below the earth's surface; (3) discharge features such as springs where uplifted bedrock with subsequent increased stream gradient and erosion has exposed underground conduits allowing the subsurface water to emerge; and (4) depositional features such as stalagmites, stalagmites, and other cave formations where calcium carbonate has precipitated from groundwater flow (Bullard 2001).

Greene County has abundant karst features including subsurface karren cutters and pinnacles, internal drainage areas, numerous losing stream segments, many springs, more than 300 caves, and over 2500 sinkholes as seen in Figure 5 (Bullard 2001). Estevelles, which act as springs when the water table is high and as swallow holes when the water table drops during dry months, are a unique geologic features present within the Wilson Creek watershed. Thomson (1986) describes two such features located along Wilson Creek near the Southwest Waste Water Treatment Plant identified as Lagoon estevelle

and Oval estevelle. Due to subsurface drainage through karst features numerous segments of Wilson Creek experience no surface flow during much of the year and watershed surface drainage divides may not reflect water source boundaries in many locations and at certain times.

SOILS

Several physical, chemical, and biological characteristics and processes contribute to the variety of soils formed within the watershed. All surfaces within the watershed are exposed to approximately the same climate, have weathered from similar parent material, and have formed within the same time frame. However, the slope and shape of basin surfaces, the density and pattern of drainage features, and the distribution of plants and animals, with their associated organic material inputs, are varied throughout the watershed and account for much of the differing soil types currently mapped.

The soils within the Wilson Creek watershed are similar to those of surrounding basins. These soils are comprised of Pleistocene loess of eolian origin over weathered cherty limestone residuum. Marbut (1910) classified them as the “Springfield Soils” of the Ozark Border Soil groups. The upper portion of the Springfield soils are composed almost entirely of silt-sized grains of various colors while the subsoils often contain up to 20% clay and are reddish in color. The general soil associations located within the study area are the Goss-Wilderness-Peridge association, the Pembroke-Eldon-Creldon association, the Wilderness-Viraton association, and to a limited extent the Keeno-Creldon association and Huntington association as seen in Figure 6 (Hughes, 1982; MSDIS, 2005).

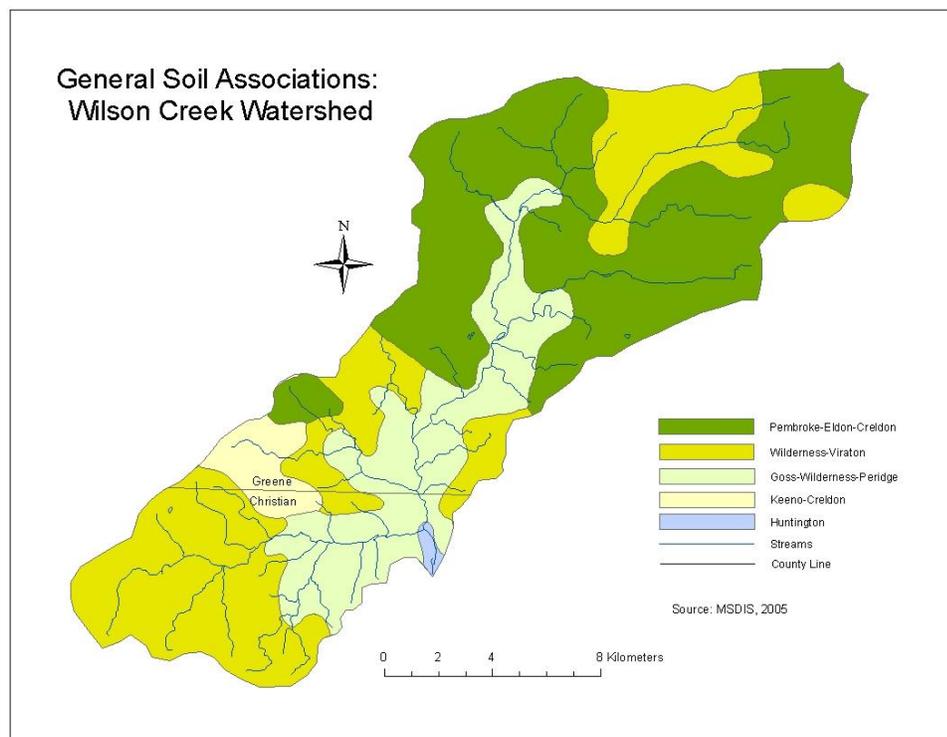


Figure 6. General soil associations within the Wilson Creek watershed.

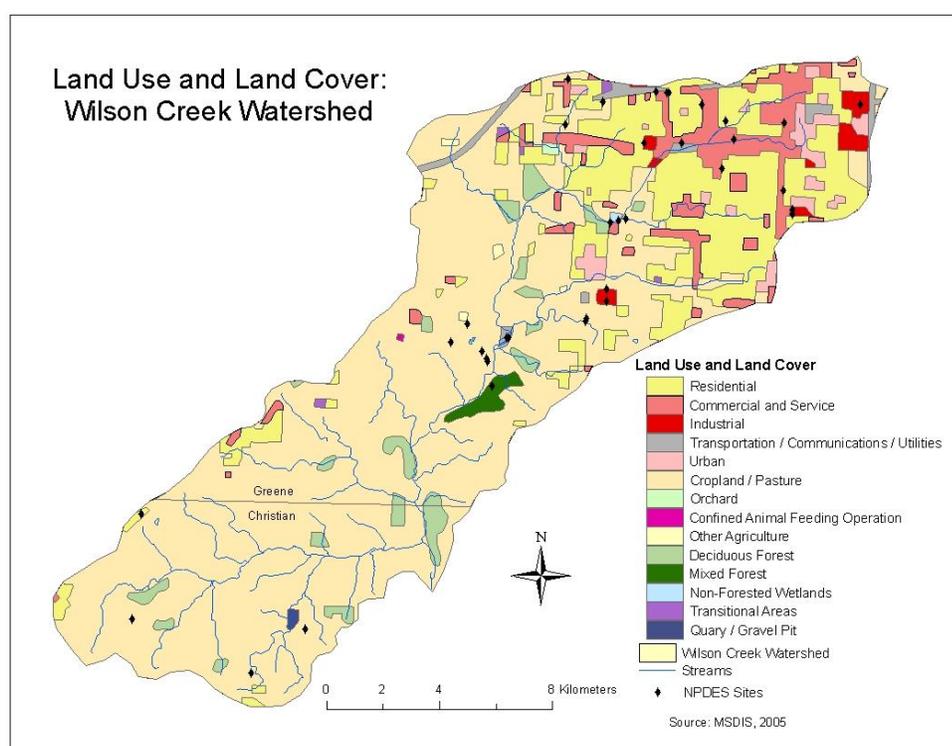


Figure 7. Land use and land cover within the Wilson Creek watershed.

The Goss-Wilderness-Peridge association consists of upland and terrace soils that are relatively deep, well drained, and range from gently sloping to moderately steep. This association makes up about 45% of Greene county soils and typically is composed of 41% Goss, 14% Wilderness, 10% Peridge, 33% other soils of very minor extent, and 2% bedrock out crop and water. These soils are well suited for grasses, legumes, and moderately well for trees (Hughes, 1982).

The Pembroke-Eldon association is also comprised of soils on upland and terrace landforms. These soils are moderately well drained and well drained and occur on gently to strongly sloping terrains. This association makes up about 23% of Greene County. The Pembroke and Creldon soils occur on much of the watershed surfaces away from the stream channels in the southern parts of Springfield (Hughes, 1982).

The Wilderness-Viraton association soils are deep and moderately well drained. They occur on gently to moderately sloped uplands and terraces. This association makes up approximately 25% of Greene County soils. While this association often comprises narrow floodplains bordering streams, the Viraton, in contrast, forms a large part of the watershed surface in northern Springfield (Hughes, 1982).

The Keeno-Creldon association has only limited extent within the watershed being found at one location in the headwaters of McElhaney Creek. These are typically shallow soils, are well drained, and occur on gently to strongly sloping surfaces. This association makes up only about one percent of Greene County soils (Hughes, 1982).

The floodplain soil units adjacent to the channel include: the Huntington silt loam, Cedar Gap silt loam, Lanton silt loam, and Hepler silt loam (Table 2)(Hughes, 1982). These floodplain silt loams are often found in association with one another and develop

under conditions of infrequent flooding (except the Cedar Gap which floods frequently), are moderately to well drained, are nearly flat (0 – 2 % slope), are moderately to very friable, and are agriculturally suitable for grasses and legumes. The upper layers are dark to very dark to 20 – 50 cm (Lanton extends to 70 cm) depth with dark grayish brown substratum extending down to approximately 1.5 meters (Hughes, 1982).

The development of floodplain soils and the sediment transported within stream channels are of particular importance for this study and are more strongly influenced by the fluvial geomorphic processes of erosion, transportation, and deposition. The streams of the basin are always at work in the construction and destruction of adjacent floodplains. Periods of geomorphic equilibrium may allow time for floodplain soils to form, while times of adjustment due to baselevel, climate, or landuse / land cover changes can remove or bury such soils. Changes in sedimentation rates due to ore extraction, land clearing, and urbanization activities have been observed to bury floodplain soils at some locations within the southwest Missouri region (Carlson, 1999; Shade, 2003). Shade (2003) measured darker color, slightly increased organic matter content, and a decrease in metal and nutrient pollutants to background levels in buried soils of the lower Wilson Creek watershed.

Table 2. Soil unit description at overbank sampling sites (Hughes, 1982).

Soil Series (Sites)	Horizon (depth in meters)	Texture	Acidity	Permeability	Avail. Water Capacity	Surface Runoff	Flood Risk	Landform
76-Hepler Silt Loam (36 & 37)	Ap (0 – 0.2) E (0.2 – 0.5) B1t (0.5 – 0.8) B2t (0.8 – 1.2) B3 (1.2 – 1.7)	silt loam silt loam silt loam silty clay loam silty clay loam	slightly acid medium acid strongly acid strongly acid strongly acid	moderately slow	high	slow	occasional	high terrace
55-Huntington Silt Loam (5)	Ap (0 – 0.3) B1 (0.3 – 0.6) B2 (0.6 – 1.2) C (1.2 – 1.5)	silt loam silt loam silt loam silt loam	neutral slightly acid medium acid medium acid	moderate	very high	medium	occasional	low terrace
54-Lanton Silt Loam (34)	A11 (0 – 0.3) A12 (0.3 – 0.4) A13 (0.4 – 0.7) C1g (0.7 – 1.1) C2g (1.1 – 1.6)	silt loam silty clay loam silty clay loam silty clay loam silty clay loam	slightly acid neutral neutral neutral neutral	moderately slow	high	slow	frequent	back-swamp
95-Cedargap Silt Loam (7, 10, & 27)	A11 (0 – 0.2) A12 (0.2 – 0.5) C1 (0.5 – 1.0) C2 (1.0 – 1.8)	silt loam silt loam v. cherty silty clay v. cherty silty clay	medium acid slightly acid slightly acid slightly acid	moderately rapid	moderate	slow	frequent	recent floodplain

CLIMATE

The mid-continent and mid latitude location of the Ozarks is more important in determining the climate of the region than its elevation and relief (Rafferty 2001). The Wilson Creek watershed is located within the Humid Subtropical climate classification near the southern boundary of the Humid Continental zone (Trewartha, 1957). The Ozark's climate is variable yet characterized by four distinct seasons with brief mild winters, long summer growing seasons, and rainfall each month of the year.

The average annual temperature for the city of Springfield is 12.8°C (55°F) with July averaging approximately 25°C (77°F) and January averaging approximately 1°C (33°F). The area receives nearly all on its precipitation as rainfall with annual totals averaging 104 cm (41 in.). On average, only 3.5% of the total precipitation (40 cm or 15.9 in.) falls as snow (Rafferty 2001).

Southerly winds are most frequent averaging 16.7 km/hr with tornados occurring nearly every year, usually between the months of April and June (Rafferty 2001). Tornadic storms can not only bring large amounts of rainfall to the watershed in a brief period of time, but can also introduce trees and other debris to stream channels affecting flow conditions and channel migration which in turn may alter sedimentation processes along the length of the stream.

HYDROLOGY

Surface Hydrology

The city of Springfield is located upon the "grand divide," as described by Shepard (1898), which roughly follows the crest of the Springfield anticline. The divide runs through northern Springfield and separates surface runoff to the north via the Sac, Osage,

and Missouri Rivers and to the south via Wilson Creek as described within the regional setting section of this chapter. Shepard described this divide as being “abrupt” in downtown Springfield where gutters at some locations along Commercial Street would route runoff on the north to the Missouri River, and on the south to the Mississippi. Wilson Creek’s average gradient is 0.2 %, with vertical relief ranging from 410 meters at the headwater tributaries of the North and South branches of Jordan Creek to 325 meters at its confluence with the James River 31 km downstream (Figure 3).

The channels of headwater streams within the Wilson Creek watershed are often well above water table height and subsequently remain dry except during precipitation events. Surface water impoundments, such as detention basins within the urban and suburban areas of Springfield and ponds within the surrounding agricultural area, are numerous within the watershed and may accelerate sinkhole development and promote subsurface drainage (Waite and Thomson, 1993). The city of Springfield (2004) maintains 1,327 km of streets ($6.8 \text{ km} / \text{km}^2$) and 1078 km of storm sewer drains ($5.6 \text{ km} / \text{km}^2$) that serve to collect, concentrate, and route surface runoff to stream channels. This effort to rapidly remove surface water from the urban areas has substantially limited infiltration thereby reducing base flow in stream channels within the watershed. This alteration of the dynamic surface-subsurface hydrologic interactions has produced wide fluctuations in the discharge conveyed within the stream channels during precipitation events.

While flooding from intense local storms can occur during any month of the year, December to June is considered the most likely months for flooding within the watershed (USACE, 1968). Based on interviews, historical documents and only two USGS gages, the U.S. Army Corp of Engineers determined that floods within the watershed are

typically short in duration and characterized by rapid rates of rise between 0.6 to 1.2 m per hour. Maximum velocities up to 3.7 m / s are typical for flood stages at most locations on Wilson Creek and its tributaries (USACE, 1968). A total of seven U.S. Geological Survey gaging stations have operated within the watershed with five collecting data during this study period (Table 3). While monthly mean discharges vary widely in magnitude and seasonality, the highest mean of monthly discharges typically occurred in May and June with the lowest occurring most frequently in August (USGS, 2004).

Karst features and urbanization within the watershed influence channel development by contributing to widely variable surface runoff rates and stream discharge measures. Subsurface drainage through sinkholes within the watershed limit the amount and alter the timing of runoff delivered to the streams during small storm events. This affects channel development yielding inconsistent channel capacity / drainage area relationships at some locations (USACE, 1968). During larger storm events when the effects of karst drainage is minimized, increased runoff from the urbanized land surface exceeds the capacity of the natural channel causing flashy discharge hydrographs, channel instability, and frequent localized flooding. This instability greatly affects the transport of water, sediment, and sediment bound pollutants through the watershed. Varying locations of stream bank and bed erosion and areas of deposition and storage along the length of the stream greatly complicate longitudinal sediment pollution signals.

Table 3. USGS gages on Wilson Creek near sampling sites.

Gage #	Description	Period of Record	Drainage Area	Average Q	Maximum Q
7052000	Near Site 34 Scenic	10/01/32 to 9/30/39; 7/11/73 to 9/22/77; 6/4/98 to present	19.40 mi ² (50.2 km ²)	18.9 cfs (0.54 cms)	6,750 cfs (191 cms) 7/12/00
7052100	Near Site 27 FR 156	9/21/72 to 8/30/82; 5/28/98 to present	35.3 mi ² (91.4 km ²)	20.5 cfs (0.58 cms)	5,480 cfs (155 cms) 7/12/00
7052152	Near Site 10 FR 168	10/1/01 to present	39.5 mi ² (102.3 km ²)	67 cfs (1.6 cms)	No data
7052150	Near Site 10 FR 168	4/01/67 to 9/30/72	47.2 mi ² (122.2 km ²)	37.2 cfs (1.1 cms)	3,700 cfs (105 cms) 12/21/67
7052160	Near Site 5 FR 182	3/1/68 to 9/30/70; 9/21/72 to 9/30/82; 8/3/99 to present	58.3 mi ² (151.0 km ²)	88.5 cfs (2.5 cms)	7,240 cfs (205 cms) 5/20/79

Q -stream discharge
cfs -cubic feet per second
cms -cubic meters per second
Source: Shade (2003)

Subsurface Hydrology

Two aquifers exist below the surface of the Wilson Creek watershed. The Springfield plateau aquifer is shallow (averaging approximately 76 m), crops out in many areas of the watershed, and consists of the rock units within the Warsaw, Keokuk, and Burlington limestones and the Elsey and Peirson formations (Waite and Thomson, 1993). The deeper Ozark aquifer, averaging approximately 275 m, consists of dolostone and sandstone layers within the Cotter dolomite and Jefferson City and Roubidoux Formations. Separating these aquifers is the Ozark confining unit. The Northview

Formation, Compton Limestone, and the Bachelor Formation make up the confining unit and consist of shale, siltstone, limestone, and sandstone layers (Waite and Thomson, 1993).

Nearly 25% of Springfield's drinking water is obtained from ground water sources. Deep municipal and industrial wells tap the Ozark aquifer which can yield up to 11,365 liters per minute. The shallower Springfield Plateau aquifer is also accessed by the city at Fullbright Spring and by many private wells within the watershed, yielding up to 91 liters per minute (Bullard, 1997). The exchange of surface water with the ground water within the Springfield Plateau aquifer can occur rapidly through sinkholes, springs and other karst conduits, thereby reducing the natural purification of infiltrating water and yielding little difference between the quality of surface and subsurface waters. Faults, improperly cased wells, and drill holes can breach the Ozark confining unit promoting the exchange of water between the two aquifers. Because of the complex surface to subsurface hydrologic linkages, the degradation of surface water within the basin can have direct adverse impacts upon the quality of water withdrawn from drinking water wells at nearly all depths and from either aquifer.

VEGETATION AND LANDUSE

Pre-settlement vegetation within the Ozarks can be roughly divided into grassy uplands, with scattered stands of oak and hickory, and mixed deciduous and evergreen forested stream valleys. Fires from natural causes and those set intentionally by Native Americans helped to maintain these grass covered upland areas that formed the eastern border regions of the Great Plains. As Schoolcraft (1821) traveled through the James

River area he described a coarse wild grass "...which attains so great a height that it completely hides a man on horseback..." As relocated tribes from the eastern United States, including the Shawnee and Delaware in the late 1700's and the Kickapoo and Cherokee in the early 1800's, began to displace the Osage Indians of the Ozarks, the frequency of wildfires was likely to be irregular (Jacobson and Primm, 1994). Without maintenance, the distribution of grasslands and forested areas were changed.

Westward expansion of white settlement during the 1800's also had a profound impact upon the area's vegetation distribution. Much of the land was placed under some form of agricultural production. Subsistence farming transitioned to general farming with the arrival of the railroad as swine, sheep, cattle, horses, milk cows, and bees were raised and corn, oats, wheat, and tobacco were produced in the area and often sold outside the region. The demand for oak railroad ties and pine lumber for the construction of growing cities led to a period of deforestation known as the Ozark timber boom, lasting until the 1920's when most of the old growth forest had been cut (Rafferty, 2001).

Today, within the undeveloped areas of the Ozarks, forests have returned to most of the stream valleys and have covered much of the once grassy uplands. The city of Springfield within the Wilson Creek watershed, however, has continued to develop and remains a regional center of economic activity. As Wilson Creek winds through this growing urban center its adjacent land area can be segregated into distinct land use / land cover categories as seen in Figure 7. The upper Wilson Creek watershed, most of which is drained by Jordan Creek, is used primarily for industrial and commercial activity. Residential and light industrial development dominates the middle stretch of the stream. Agricultural uses including cattle grazing and hay production are wide spread in the

middle to lower reaches from HWY 60 (Sunshine Rd.) to the northern boundary of the Wilson Creek National Battlefield Park (Figure 3). A return to the pre-settlement oak-hickory and grassland vegetation has been encouraged in the lower reaches of the stream within the Wilson Creek National Battlefield Park.

These settlement associated changes in vegetation distribution and land use within the stream valleys of the watershed have contributed to the present day shape and composition of the channel and adjacent floodplain of the Wilson. Jacobson and Primm (1994) have attributed instability and coarse sediment aggradation within the channels of Ozark streams to increased timber harvest and agricultural activities that accompanied population growth during settlement. Geomorphic responses to changes in the hydrologic and sediment budgets can be seen in the coarse chert gravel beds, the absence of deep residual pools, the incised form of the channel, and the deep silty overbank terrace deposits within the Wilson Creek watershed. Changes in land use since the early 1800's have not only altered the distribution and abundance of vegetation within the watershed, but have also modified stream channel characteristics and adjusted the sediment erosion, transport, and deposition processes at work within the streams.

SPRINGFIELD HISTORY

The first white settlers to what is now known as Springfield came from Tennessee in the late 1820's. The Campbell, Fulbright, Miller, and Burnett families settled in the upper Wilson Creek watershed near the spring fed and free flowing Jordan Creek (Rafferty, 2001). Abundant water resources and comparatively flat land attracted many more settlers to the area within the next decade as Springfield became the Greene County seat in 1833 and the location of the federal land office for southwest Missouri in 1835.

Springfield incorporated in 1838 and by 1859 the population had grown to twenty-five hundred. The arrival of the St. Louis / San Francisco and Atlantic and Pacific Railroads in the 1870's prompted a period of accelerated growth as Springfield became the transportation, manufacturing, livestock and grain distribution, and population center for the entire Ozarks region (Rafferty, 2001).

Through the early and mid 1900's Springfield continued to grow with a population exceeding sixty thousand by mid century. Much of the industrial and manufacturing activity during this time occurred along the banks of Jordan Creek between Glenstone Avenue and Kansas Expressway (Scheibel, 2000). Increased runoff from expanding impervious area caused frequent flooding within the Jordan Valley. This prompted the Public Works department of Springfield to build an underground channel to contain Jordan Creek from Main Street to Washington Avenue between 1928 and 1934. Much of the remaining channel segments in the upper watershed were channelized with stone or concrete to eliminate lateral migration and increase the stream's capacity to remove the increasing storm water runoff and waste flow generated within the growing city (Scheibel, 2000).

The rapid growth of Springfield continued into post-World War II period. As population climbed, the city generated an increasing amount of waste water. In 1959 the SW WWTP began operation at its current location on Wilson Creek, 12.2 km from its confluence with the James River. Formerly, waste water had been treated at a facility near Bennett and Scenic Roads and Wilson Creek which was used as a landfill between 1955 and 1961 as water treatment was transferred over to the new plant (Sutton, 1981). The construction date of this earlier treatment plant is unknown. The SW WWTP

currently treats the waste water from most of Springfield and also from the surrounding towns of Battlefield, Brookline, and Strafford (Black, 1997). An upgrade was made in 2001 to reduce phosphorous loading to Wilson Creek, but no improvements have been made in recent years related to mercury removal (Holdt, 2005).

The industrialization and urbanization of Springfield also increased in the post-war period. Manufacturing and processing operations continued to locate and expand within the watershed including companies such as Kraft Cheese, Paul Mueller, City Utilities, Lily-Tulip, Hoerner Box, Royal Mcbee, Dayton Rubber Company, Kennedy Brick and Steel, Litton Industries, Loren Cook Company, Positronic Industries, Springfield Tablet Manufacturing Company, Zenith Radio Corporation, 3M corporation, Ralston Purina, MD Pneumatics, General Electric Company, RT French, and others as chronologically documented by Shade (2003). These companies, and a growing population exceeding two hundred thousand (MCDC, 2000), have not only produced a stream of economic goods and services flowing from Springfield, but many have also contributed to the flow of waste from the city within the waters of Wilson Creek.

SUMMARY

The Wilson Creek watershed is unique in a regional context as a growing urban service center with a long industrial and manufacturing history and in a broader context as an area of uplifted karst terrain. The fairly uniform limestone geology of the watershed reduces variability in stream sediment composition providing good contrast to anthropogenic inputs. The karst topography, however, increases surface and subsurface hydrologic complexity, producing stream reaches of intermittent flow and subsequent spatial and seasonal variability in sediment transport and deposition regimes. The mild,

humid mid-latitude climate allows abundant riparian vegetation, developed soils, and seasonal organic detritus inputs to the aquatic environment affecting trace metal accumulation, methylation, and transport. Finally, wide spread land-clearing and settlement activities in the early 1800's, and subsequent industrialization in the upper watershed produced geomorphic channel and floodplain responses, such as channel enlargement and spatial / temporal changes in sedimentation rates, and degradation of the aquatic environment as measured in trace element pollution in the stratigraphic sedimentary record. Although a few unique characteristics help define the Wilson Creek watershed, common elements of human history and natural fluvial processes insure the applicability and benefit of research findings to many urban centers with natural drainage features.

CHAPTER FOUR:

METHODS

Assessing the spatial and temporal distribution of pollutants in the channel and overbank sediments of Wilson Creek required a methodology involving field techniques and laboratory procedures. Field methods involved the collection of channel, overbank, and watershed surface sediment samples and topographic channel survey data.

Laboratory methods consisted of the preparation and analysis of sediment samples for chemical composition, radiometric dating, and texture characteristics and the storage, analysis, normalization, analysis of sampling and analytical error, and graphical / cartographic rendering of resulting data.

FIELD METHODS

Sample Collection

Two hundred forty samples were collected between September 2002 and May 2004 at 66 locations (Figure 8) from channel, overbank, and land surface sediment to capture the geographic distribution of mercury within the watershed. Active channel sediment samples were collected at 42 main channel sites and 16 tributary channel sites. Overbank samples were collected at eight of these locations along the main channel and one along a tributary. Surface samples were collected at four sites in the upper watershed and four within the lower. In addition, 33 samples were collected from five previously sampled overbank sites for ¹³⁷cesium dating and 24 samples from four previously sampled main channel sites for quality assurance purposes and to assess the temporal continuity of the data. All samples were collected by hand using a small trowel, consisted of approximately 50 - 100 g (1.5 kg for cesium samples) of sediment, and were placed into

resealable polyethylene storage bags for transport to the SMSU Geomorphology lab for processing and analysis.

Channel Samples

Active channel sediments were collected from bankfull floodplain surfaces (Figure 9) and low energy depositional zones at stages below bankfull (Hakanson, 1984) such as point bar tails, pools, and obstruction eddies at approximately one-kilometer intervals along the 32 km main channel. Sampling resolution was increased near the Southwest waste water treatment plant (SWWTP) with collection at 100 meter intervals up and downstream of the outflow and within South Creek (Figure 10). Previous studies and early stages of this study suggested that mercury enrichment was occurring in the vicinity of the SW WWTP. These samples were collected to determine where sediment enrichment was occurring at the reach-scale. It was expected that these transient deposits would aid in the identification of both point and non-point mercury sources.

Fine sediments from low energy areas were also collected from 16 tributary locations from four tributaries in the upper watershed and four in the lower. Upper watershed tributaries included two within the historical industrial area and two from residential neighborhoods. Three tributaries draining land surfaces around the Southwest power plant (SWPP) and one near the SWWTP outflow were selected in the lower watershed. Tributaries draining these key locations were sampled in an effort to isolate the geographic distribution of mercury inputs from watershed surfaces, differentiate atmospheric deposition from historical and recent discharge to streams, and aid main channel mercury distribution understanding.

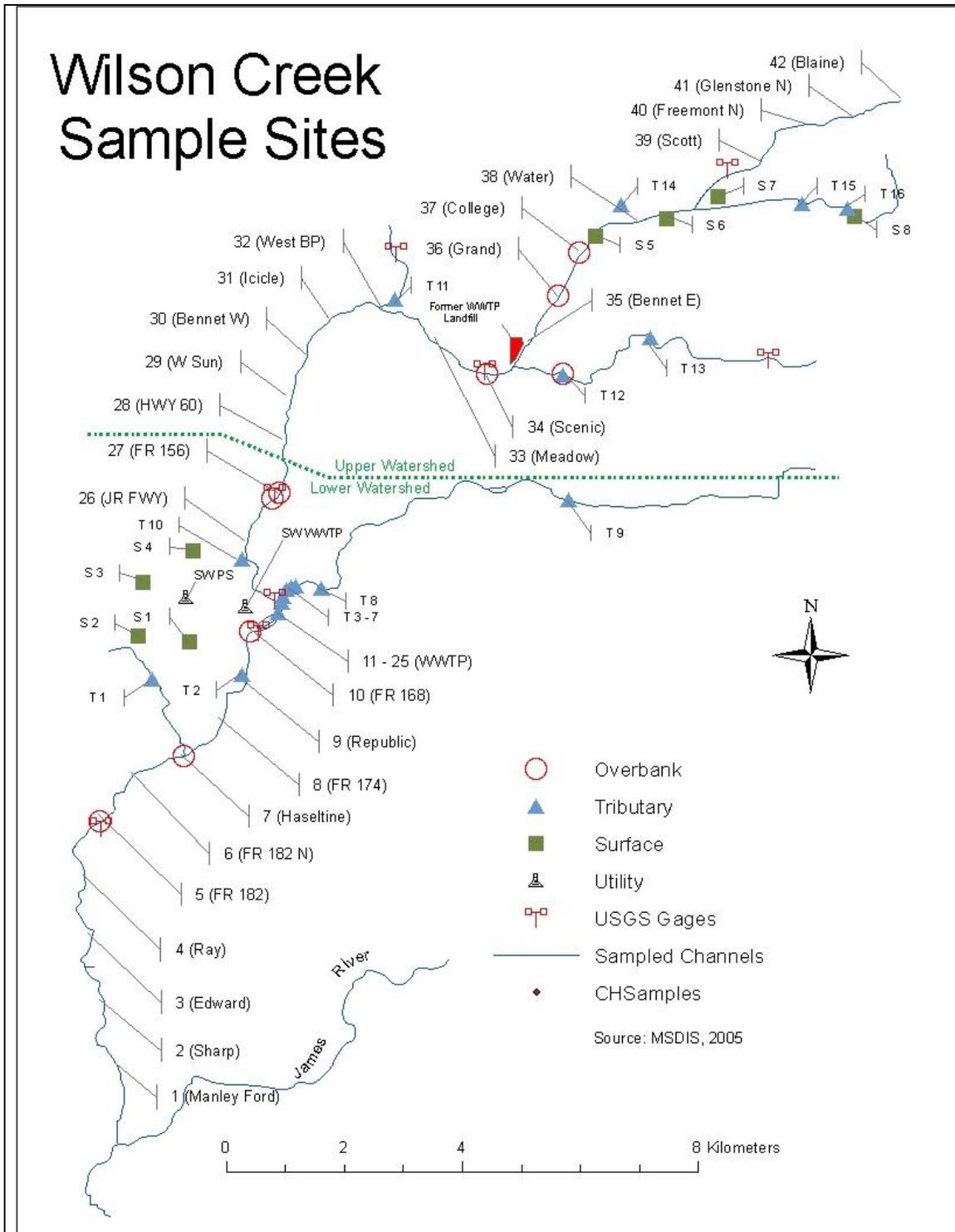


Figure 8. Sample locations along Wilson Creek and selected tributaries.

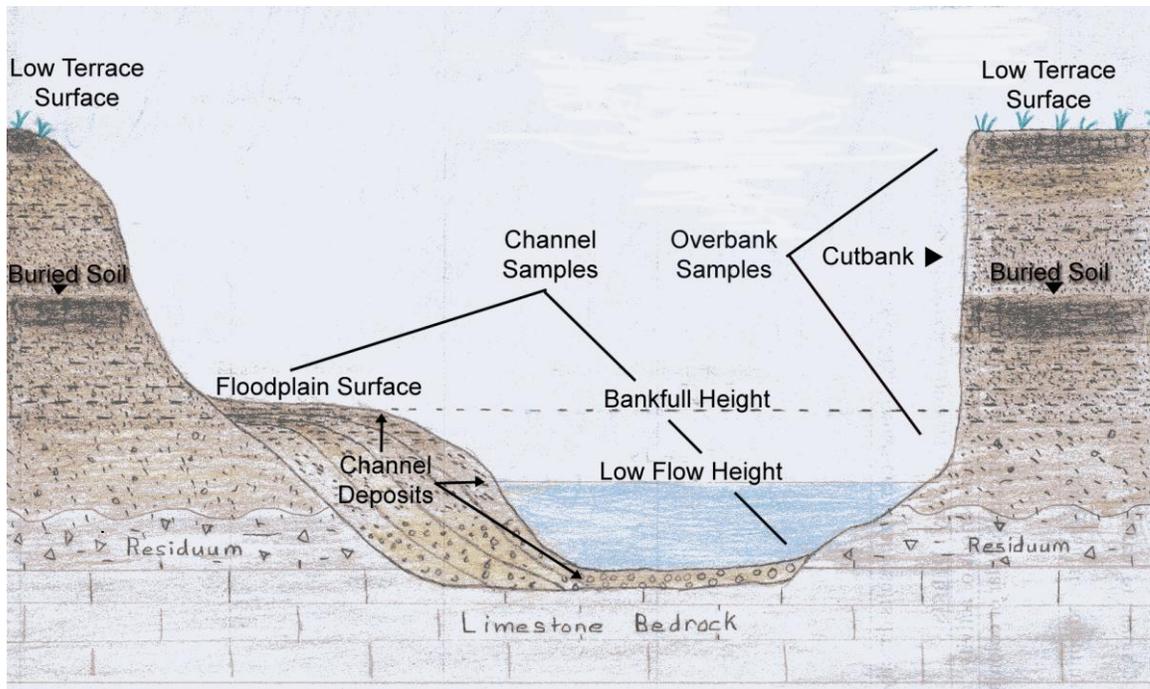


Figure 9. Stream cross-section diagram.

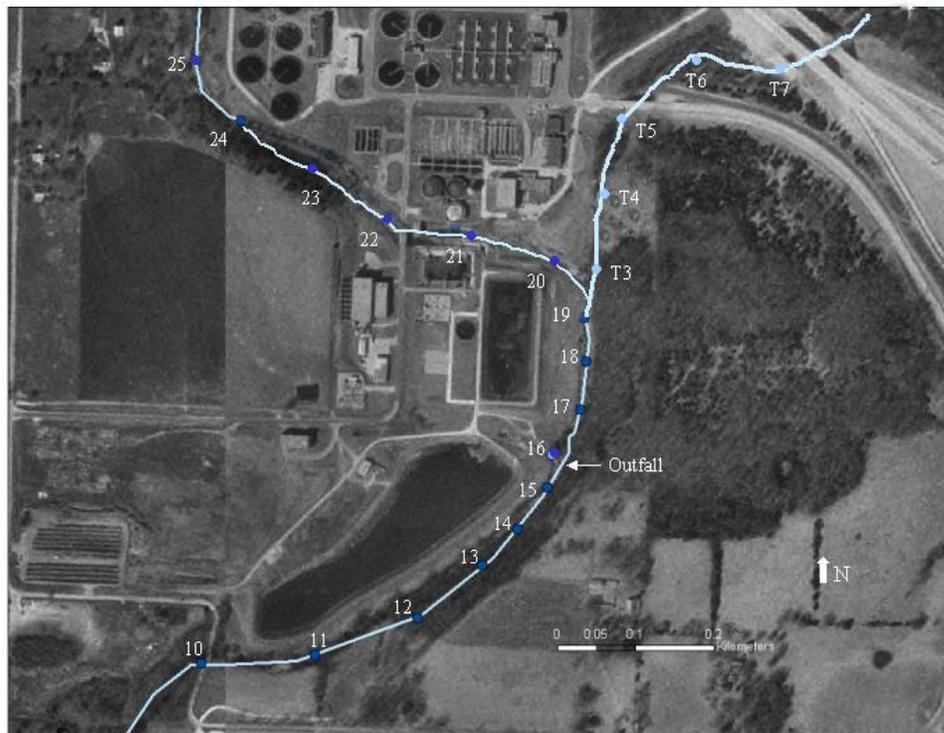


Figure 10. Sample locations near the SW WWTP.

Replicate Channel Samples

Temporal replicate samples were collected for five month (1/03 – 6/03), sixteen month (1/03 – 5/04), and nineteen month (10/02 – 5/04) periods at sites 5 & 10, 5 & 36, and 27 & 34 respectively (Figure 8). The May 2004 samples for the 16 and 19 month replicates were collected in triplicate for both low flow deposits and bankfull surfaces at each of the four sites. The replicate samples provide a means of assessing the degree of spatial heterogeneity among channel deposits and temporal continuity of the geochemical or contaminant signal for sediment sampling periods separated by the occurrence of flood events.

Overbank Samples

A total of nine overbank floodplain profiles were sampled in this study (Figure 8). One tributary site and three main channel locations downstream of the historical industrial area were selected in the upper watershed. Five overbank profiles were sampled in the lower watershed at four locations. Samples were collected from cutbank erosional features adjacent to the channel. Overbank profiles were sampled in 10 cm units from the low terrace floodplain surface to the depth of buried point bar deposits or valley floor residuum. This depth ranged from 1 to 2 meters at all sites except for the most upstream location with an overbank deposit thickness of only 45 cm on top of point bar deposits. Additional overbank samples of 1.5 kg each were collected at five of these sites to depths 60 and 70 cm for radiometric dating. Sediment stored in overbank deposits provides information on historical pollution transport trends and peak storage locations, sedimentation rates, and possible remobilization potential.

Watershed Surface samples

Samples from the watershed surface were collected at eight locations within the watershed (Figure 8). Upper watershed sediment samples were collected at four street locations on the low terrace surface within the historical industrial area. Curb cuts and street gutter sites were selected for sampling where fine-grained sediment had accumulated and was expected to have a short residence time. These samples were expected to reveal current pollution contribution from both eroded industrial soils and atmospheric deposition. This information will help determine if the source of mercury to the channel is from recent land surface contribution or from eroded industrialization-era bed and bank material.

Four lower watershed surface samples were collected within 700 meters of the SWPP complex in the northwest, northeast, southeast, and southwest directions (Figure 8). These samples consisted of a mixture of the top 5 cm of soil from grassy areas at least 10 meters from nearby roads. These samples were expected to indicate close proximity atmospheric mercury deposition from power plant emission stacks. Such information may explain mercury concentration in nearby channel samples as being from non-point land surface erosion or from other sources.

Channel Cross-section surveys

Topographic channel cross-section surveys were performed at each of the nine overbank sample sites. Survey data consisted of relative elevation values at corresponding channel width distances. Data was collected at approximately one meter intervals between low terrace banks across the channel capturing each substantial topographic variation. Observed bankfull height and water's edge elevations were noted.

Cross-section survey data was collected to assess geometric channel variations within the watershed. Three U. S. Geological Survey stream gages recorded stage and discharge data during the study period at sites 5 (FR 182) in the lower watershed, site 28 (FR 156) in the middle watershed, and site 34 (Scenic) near the upper watershed (Figure 8).

LABORATORY METHODS

Sample Preparation

Each sediment sample was air dried in the SMSU geomorphology laboratory for at least 24 hours and then oven-dried at 60° Celsius (C) until moisture content was negligible. Samples were then disaggregated by hand using a pestle and mortar noting and removing large particles of gravel and organic matter (OM). Sediment and soil samples were passed through a 2 mm stainless steel sieve and the < 2 mm fraction retained in the original storage bags for further analysis.

Geochemical Analysis

Geochemical analysis of 268 five-gram sub-samples was contracted to ALS Chemex laboratories in Sparks, Nevada. Total mercury concentrations were determined in these samples using cold vapor atomic absorption spectroscopy (CVAAS) with a detection limits of 10 – 100,000 ppb. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to measure the concentration of 33 additional elements with detection limits shown in Table 4. Sample preparation for ICP-AES and CVAAS analysis was completed using a 3:1 mixture of hydrochloric and nitric acids known as aqua regia digestion. This digestion procedure is useful for volatile elements, such as mercury which is reduced to its elemental (Hg^0) state, and releases solubilized elements in all but the most resistant silicate minerals and organic materials.

Table 4. Thirty-four analyzed elements and detection ranges (ppm).

Ag	0.2 - 100	Fe	0.01% - 15%	S*	0.01 - 10%
Al*	0.01% - 15%	Ga*	10 - 10,000	Sb*	2 - 10,000
As	2 - 10,000	Hg	0.01 - 100	Sc*	1 - 10,000
B*	10 - 10,000	K	0.01 - 10%	Sr*	1 - 10,000
Ba*	10 - 10,000	La*	10 - 10,000	Ti*	0.01 - 10%
Be*	10 - 10,000	Mg*	0.01% - 15%	Tl*	10 - 10,000
Bi	2 - 10,000	Mn	5 - 10,000	U	10 - 10,000
Ca*	0.01% - 15%	Mo	1 - 10,000	V	1 - 10,000
Cd	0.5 - 500	Na*	0.01 - 10%	W*	10 - 10,000
Co	1 - 10,000	Ni	1 - 10,000	Zn	2 - 10,000
Cr*	1 - 10,000	P	10 - 10,000		
Cu	1 - 10,000	Pb	2 - 10,000		

* Digestion incomplete for most sample matrices.

Source: ALS Chemex Laboratories, 2004 (package ME-ICP41m)

Organic Matter

All samples were tested for organic matter content using an in-house loss on ignition (LOI) technique modified from Pavlowsky (1995) and Dean (1974). Previous triplicate analyses using this method have been consistently precise with a standard deviation of 0.04% and coefficient of variation less than 1% (Shade, 2003). Five gram sub-samples were placed in porcelain crucibles (30 samples per run), dried for 2 hours at 105° C to reduce atmospheric moisture, and weighed. These were the “pre-burn” sediment and crucible weights (A). Samples were then placed into a muffle furnace, heated at 600° C for 6 hours, and weighed (Figure 11). These were the “post-burn” sediment and crucible weights (B). The differences between the pre- and post-burn sediment and crucible weights were divided by corresponding pre-burn sediment-only weights (C). This value was multiplied by 100 to obtain the OM percent LOI as shown in the equation below:

$$\text{OM\% LOI} = [(A - B) / C] * 100$$

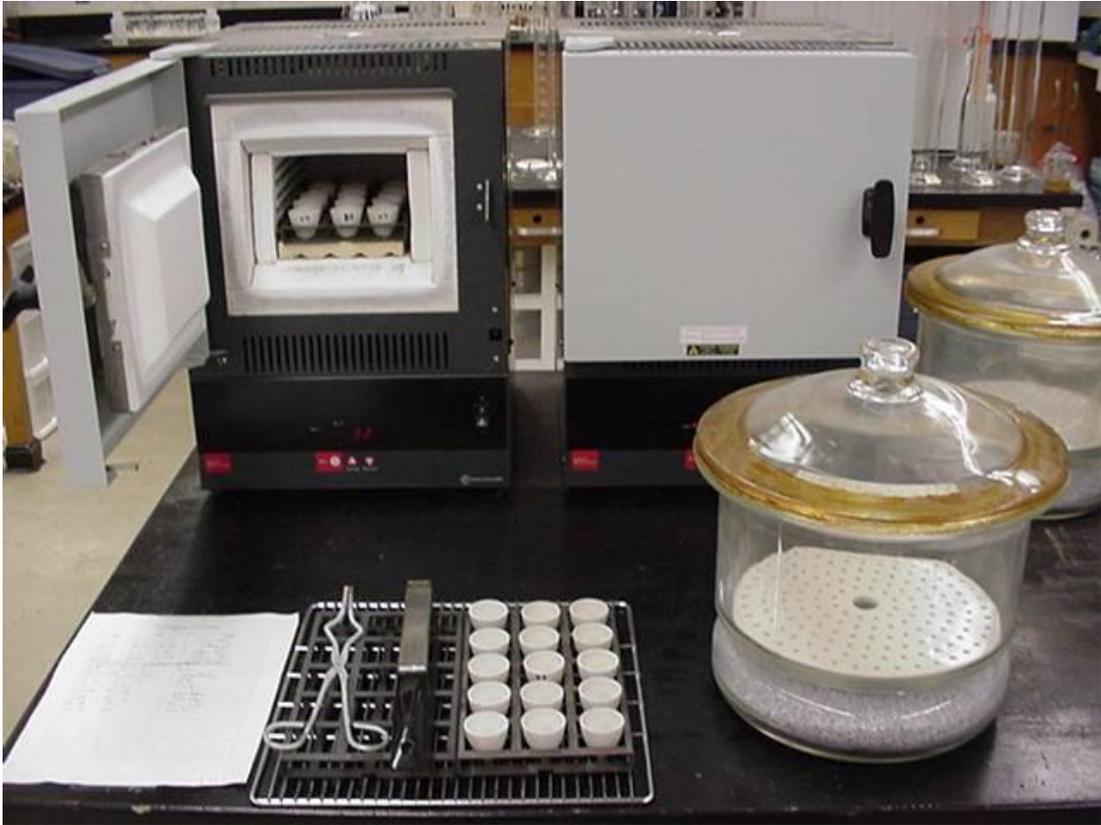


Figure 11. Muffle furnaces in the SMSU Geomorphology lab.

Radiometric Dating

Dr. Jerry Ritchie with the Agricultural Research Service Hydrology Remote Sensing Laboratory, United States Department of Agriculture performed 137 cesium analysis on 33 overbank samples. 137 Cesium activity was determined by spectroscopic gamma ray analysis with concentration estimates reported in Becquerels per Kg (Bq/Kg) (Shade, 2003).

The presence of 137 cesium in the soil profile is the result of atmospheric deposition from nuclear weapons testing in the 1950's and 1960's. Once deposited, 137 cesium adsorbs strongly to surface sediment and remains relatively stationary in the stratigraphic profile with only minor mixing due to bioturbation. Dating sedimentary deposit profiles

can be done by assigning a 1954 date to the sediment layer of first ¹³⁷cesium occurrence and a 1964 date to the layer in which ¹³⁷cesium activity peaks (Shade, 2003).

Sediment Texture Analysis

Sediment texture analysis was performed on a small subset (n = 27) of samples to determine the suitability of aluminum as a proxy measure of the clay fraction for all samples. Three samples with low aluminum, three with moderate, and three with high aluminum percentages were selected from three different depositional environments: channel sediment, post-settlement overbank sediment (above the observed buried soil), and pre-settlement overbank sediments (below the observed buried soil).

The hydrometer method was selected to determine the percentages of sand, silt, and clay within the samples using an in-house technique modified from Gee and Bauder (1986). Previous triplicate analyses using this method have been consistently precise with a standard deviation of less than one percent and averaged coefficient of variation less than four percent (Shade, 2003). The samples were pretreated to reduce the organic matter content and to separate mineral and organic particles within the samples. This was accomplished by digesting the samples in a solution of deionized water, 5 % glacial acetic acid, and 30 % hydrogen peroxide. After digestion the samples were dried, weighed, mixed with a dispersant solution of sodium hexametaphosphate, and diluted to one liter with deionized water in a graduated cylinder (Figure 12). After suspending the sediment in the solution by mixing, hydrometer readings were recorded at the time intervals corresponding to the settling velocities of particles at the sand-silt boundary of 63 μm , the silt-clay boundary of 2 μm , and the clay-fine clay boundary of 1 μm based on

Stoke's law. Percent sand-silt-clay was calculated from the timed readings according to the following equation:

$$\text{Percentage} = (\text{corrected hydrometer reading} / \text{dried sample mass}) * 100$$

The samples were then wet sieved to retain the $> 63 \mu\text{m}$ sand fraction. This fraction was dried, weighed, and used for hydrometer reading sand percentage correction.



Figure 12. Sediment suspended in one liter cylinders for hydrometer readings.

DATA ANALYSIS

Computer Software

Resulting data from topographic channel cross-section surveys and geochemical, radiometric, and textural analysis of sediment samples was stored, processed, and graphically displayed using Microsoft Excel 2000 software. Excel was used to calculate OM% LOI, percent sand-silt-clay, correlation coefficients, and mean concentrations of elements from multiple samples at a single sample site and at above and below buried soil depths within overbank units. Spatial data was obtained from Missouri Spatial Data Information Service (MSDIS) and collected using a Garmin 12 GPS receiver and subsequently stored, processed, and displayed using ESRI ArcMap version 9 software. Multiple regression analysis in SPSS statistical analysis software was used to perform step-wise techniques to evaluate the role of geochemical substrates in decreasing variation in pollutant concentration (Horowitz et al., 1989). Microsoft Power Point and Adobe Photoshop software was used to create flowcharts and diagrams.

Normalization

Data normalization was used for sediment-mercury analysis in channel samples to enhance source identification effectiveness. Aluminum normalization is commonly used in geochemical studies to reduce the spatial effects of granular variability and dilution by silicates such as sand (Din, 1992; Horowitz, 1991; Piper, 1973). This owing to the conservative element's ubiquitous abundance within the earth's crust and its presence in the crystal structure of common clay minerals. Normalization was accomplished by the use of a simple ratio:

$$\text{Normalized ratio} = \text{Hg ppb} / \text{Al \%}$$

ANALYTICAL AND SAMPLING ERROR

Geochemical analysis

Four samples, one from each of four different sites, were selected for within-sample duplicate (n = 2) analysis to assess sample heterogeneity and analytical error. The mean, standard deviation, and coefficient of variation (CV) were calculated for five geochemical substrate elements (Al, Ca, Fe, Mg, & Mn) and four selected pollutant elements (Cu, Hg, Pb, & Zn) and are reported in Appendix I with a summary shown in Table 5. Overall CV values were less than or equal to 21 % for the selected elements with five being 9 % or less. Mercury CV values of 2 to 6 % were calculated from replicate sample data collected by Gray (2003), analytical precision for mercury at ± 10 % was reported by Horowitz et al. (1989), and Paulson (2004) reported a relative percent difference of up to 40 % for replicate samples of mercury. Mercury CV of 19.1 % reported here and the CV values for the other elements reported in Table 5 are good considering that more than 16 months had elapsed between the analysis of the original sample and that of the duplicate sample in each set. Duplicate analysis was evenly divided between higher and lower mercury concentrations as compared to the original sample.

Table 5. Variations in geochemical analysis at four sample sites (n = 2).

	Al	Ca	Fe	Mg	Mn	Cu	Hg	Pb	Zn
	%	%	%	%	ppm	ppm	ppb	ppm	ppm
<u>Overall</u>									
Mean	1.5	3.8	2.1	0.2	1652	34	221	79	218
St.Dv.	0.3	0.5	0.1	0.04	94	5	27	8	26
CV%	21.0	6.2	5.6	20.4	7.1	12.1	19.1	7.0	8.7

Spatial Heterogeneity

Spatial heterogeneity of geochemical substrates and selected pollutant elements within low flow and bankfull deposits was assessed at four sites. Sites 34 and 36 were sampled in the upper watershed and sites 5 and 27 were sampled in the lower watershed. At each site three samples were collected from low flow deposits, such as point bar tails, and three samples from bankfull surfaces. Each sample was spaced approximately 2 to 3 meters apart parallel to the stream. The mean, standard deviation, and coefficient of variation were calculated with summary results shown in Table 6 and complete analysis shown in Appendix II. The channel deposits show a low degree of spatial heterogeneity with CV values similar to those of within sample analysis. All CV values averaged below 26 % with iron and magnesium having values less than 10 percent. These findings are similar to within-site variability determined in a nation-wide study for selected physical sediment characteristics for which variation less than 10 percent required between 8 and 339 samples (Suedel and Rodgers, 1991). Variability in OM and Al substrates can affect pollutant levels due to substrate sorbtion capacity. In general, the CV values for the site variability are 0.5 to 2 times those of within-sample variability.

Table 6. Site heterogeneity in substrate and pollutant concentration for channel deposits.

	OM %	Al %	Ca %	Fe %	Mg %	Mn ppm	Cu ppm	Hg ppb	Pb ppm	Zn ppm
Minimum	6.2	0.8	0.8	1.7	0.1	662	15	30	29	79
Maximum	18.1	1.9	12.0	3.2	0.3	3260	74	330	324	517
Overall										
Mean	10.3	1.5	6.2	2.3	0.2	1889	43.4	221.7	126.6	342.8
St.Dv.	1.8	0.1	1.3	0.2	0.02	208.0	7.2	50.0	30.2	60.2
CV %	17.2	11.1	21.2	9.1	9.6	12.2	16.5	25.6	18.2	18.2

The coefficient of variation was also used with these same 24 samples to compare spatial variation between low flow and bankfull deposit concentrations of Cu, Hg, Pb, Zn, and corresponding Al-normalized ratios. The summary statistics for this comparison are reported in Table 7 with full analysis shown in Appendix III. The degree of heterogeneity is similar between both types of channel deposits yet the bankfull surface is consistently more variable. Lower CV values for the low flow channel samples may indicate frequent mixing within these more mobile deposits. The less frequent high discharge events, with increased suspended sediment load, may be creating a floodplain with a more diverse spatial deposition distribution. The use of aluminum to normalize data for grain size variability did not reduce CV values in low flow or bankfull deposits. All CV values were greater for the normalized data except for mercury in the low flow deposits which was reduced by 1 percent.

Table 7. Variation of concentration of selected pollutant elements and Al ratio values in low flow and bankfull deposits at sites 5, 27, 34, and 36.

Landform Deposit	Cu *	Cu/Al	Hg**	Hg/Al	Pb*	Pb/Al	Zn*	Zn/Al
Low Flow								
Mean	39	30	193	139	109	90	318	256
St.Dev.	5	5	38	26	17	14	50	44
CV %	13	16	24	23	15	17	16	19
Bankfull								
Mean	48	34	251	178	145	112	368	267
St.Dev.	9	10	62	59	44	45	71	75
CV %	20	24	28	31	22	24	20	24
Overall								
Mean	43	32	222	158	127	101	343	261
St.Dv.	7	7	50	42	30	30	60	60
CV %	17	20	2	27	18	21	18	21

* Concentrations in ppm. **Hg concentrations in ppb.

Temporal Continuity

The comparison of geochemical data in channel deposits from samples collected at the same sites at dates spanning a nineteen month time period was done to investigate the degree of change in element concentrations with time. Temporal continuity within channel samples was assessed by calculating the coefficient of variation for samples collected on different dates at the same sites. Replicate samples were collected for five month (1/03 – 6/03), sixteen month (1/03 – 5/04), and nineteen month (10/02 – 5/04) periods at sites 5 & 10, 5 & 36, and 27 & 34, respectively. Summary results for the geochemical substrates OM, Al, Ca, Fe, Mg, and Mn are shown in Table 8 and for the selected pollutant elements Cu, Hg, Pb, and Zn (Cd omitted because reported values were close to the lower detection limit) and associated Al normalized ratios in Table 9. Temporal replicate sample calculations for the five month, sixteen month, and nineteen month periods can be found in Appendix IV, V, & VI. Figure 13 shows the temporal variability in mercury at five sites during the study period.

The variation in geochemical substrates in channel deposits within the sampling period is minimal and does not appear to increase with increasing time. The range in CV percent varied little between the five month (10.4 – 30.3), sixteen month (6.1 – 33.6), and nineteen month (5.4 – 33.3) time periods. The OM variability remained relatively high in all three time periods (> 24.5 %), while Fe variability remained relatively low (<10.4). The greater OM variation may be due to the seasonal differences in organic detritus input to the stream environment (e.g. leaves).

Table 8. Temporal variation in geochemical substrates.

Time Period	Sites		OM %	Al %	Ca%	Fe%	Mg%	Mn ppm
Five Month {1/03 (n = 3) - 6/03 (n = 3)}	5 & 10	Mean	9.1	1.5	3.9	2.1	0.1	1727
		St.Dv.	2.9	0.3	0.7	0.2	0.0	621
		CV %	30.3	23.9	16.8	10.4	31.3	32.1
Sixteen Mo. {1/03 (n = 3) - 5/04 (n = 6)}	5 & 36	Mean	8.5	1.3	4.6	2.0	0.2	1310
		St.Dv.	2.9	0.3	0.3	0.1	0.0	263
		CV %	33.6	25.6	6.1	6.5	23.5	20.2
Nineteen Mo. {10/02 (n = 3) - 5/04 (n = 6)}	27 & 34	Mean	9.9	1.3	6.5	2.4	0.2	2229.2
		St.Dv.	2.3	0.1	1.4	0.2	0.0	136.7
		CV %	24.5	9.1	33.3	9.9	5.6	5.4

The variation in pollutant concentration in channel deposits within the sampling period is slightly higher than that for the geochemical substrates. Most elements had CV values less than 27 % with only Hg (34.5 %), Pb (35.2 %), and Cu (44.5 %) having slightly more variation. Variability does not, however, appear to increase over the sampling period. The range in CV percentage decreased over the five month (26.6 – 44.5), sixteen month (21.4 – 26.6), and the nineteen month (18.6 – 23.5) time periods.

Aluminum normalized ratios for the selected pollutant elements were generated to compare variability over time while accounting for grain-size related sorting. Normalization tended to have little effect on variability, producing minimal increases and decreases in CV percent (2 – 11 %) for most elements. Some changes were more substantial as seen in normalized Pb CV percentages increasing by 30 % in the nineteen month period, and decreasing for Cu over five and sixteen months and for Zn during the sixteen month period.

Table 9. Temporal variation in concentration (ppm) and Al ratio of pollutant elements.

Time Period		Cu	Cu/Al	Hg*	Hg/Al	Pb	Pb/Al	Zn	Zn/Al
Five Month (1/03 – 6/03) (Sites 5 & 10)	Mean	44	28	390	289	99	80	232	164
	St.Dv.	19	9	130	90	38	42	62	39
	CV %	44.5	31.1	34.5	36.1	35.2	46.3	26.6	24.6
Sixteen Month (1/03 – 5/04) (Sites 5 & 36)	Mean	38	32	231	206	106	99	266	240
	St.Dv.	9	4	49	85	25	13	57	26
	CV %	24.8	10.8	26.6	34.5	21.4	17.5	23.0	9.7
Nineteen Month (10/02 – 5/04) (Sites 27 & 34)	Mean	44	38	186	155	115	31	344	301
	St.Dv.	7	10	34	36	20	20	49	50
	CV %	18.6	23.9	23.0	28.3	23.5	53.6	20.3	22.7

* Hg concentrations in ppb

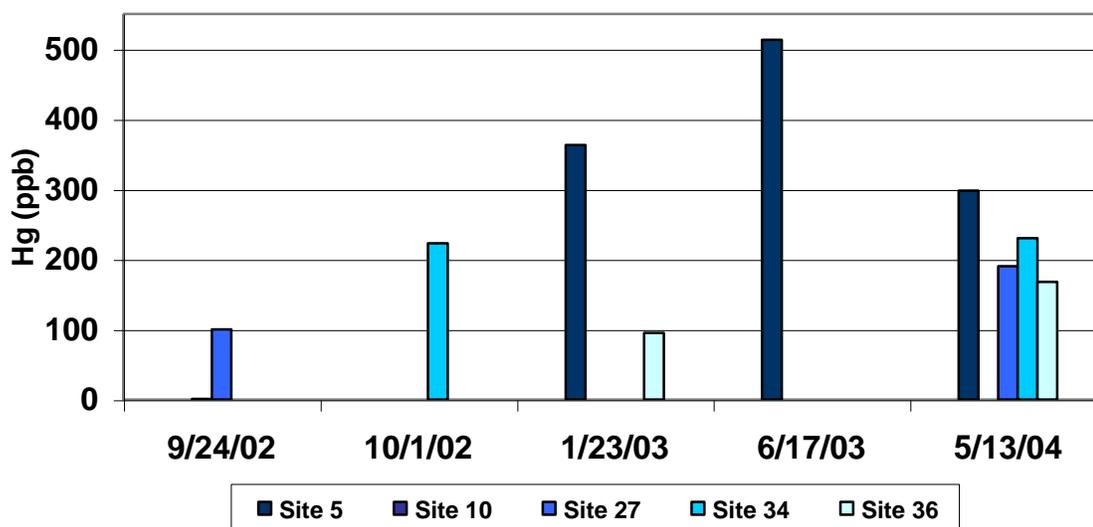


Figure 13. Mean mercury concentrations at five sites for different sampling dates.

Changes in metal concentrations in the channel sediments of Wilson Creek during the nineteen month study period were minimal even when controlling for grain-size related sorting (Figure 13). This stands in contrast to the findings of Waslenchuk (1975) who estimated that Hg content exponentially decreased at 50 percent annually in the Ottawa River near Ottawa, Canada. This difference is to be expected since the Ottawa is a large river transporting most of its Hg load during low flow conditions as suspended sediment. Wilson Creek, however, is a small Ozark stream that typically mobilizes its bed sediment only during increased flow conditions. While some degree of variability in metal concentrations in channel samples is to be expected in fluvial systems where seasonal high flow discharges transport and deposit constituent bearing sediment, the small variation among the replicate channel samples over the nineteen month study period lends credibility to the temporal stability of the geochemical data used in this study.

Summary

Within-sample duplicate analysis indicated that sample heterogeneity and analytical error was low. CV values were generally less than 20 %, with more than half of the elements tested having CV values less than 9 %. Within-site triplicate analysis indicated low spatial variability at sample locations. All CV values were less than 26 % and were generally 0.5 to 2 times the corresponding within sample CV percentages. Variability in geochemical substrate and pollutant concentrations at each site was also low over the time interval of the study period with CV % typically less than 30 percent. This indicates that pollutant source and supply rate was relatively constant over the 19 month study period. The use of aluminum ratios to account for grain-size sorting effects did not reduce variability as expected and actually increased CV values for each pollutant.

CHAPTER FIVE:

RESULTS AND DISCUSSION

This chapter will present and discuss the findings from physical and geochemical investigations into the stream channels and sediment of channel, overbank, and surface deposits within the Wilson Creek watershed. Information will be organized into the following sections: (1) geomorphology and sedimentology, describing basin profile, channel cross-section surveys, channel discharge capacity, two-year flood, sediment texture and data normalization, organic matter content, sedimentation rates, and buried soil surfaces; (2) sediment geochemistry, describing mercury – substrate associations, overbank deposits, and channel deposits; and (3) mercury distribution, describing spatial distribution in channel and overbank environments, temporal distribution, mercury source identification, and implications. Appendix VII lists geochemical data for each sample.

GEOMORPHOLOGY AND SEDIMENTOLOGY

Basin and Channel Characterization

Basin Profile. Wilson Creek, including the Jordan Creek tributary, has a basin slope of 0.0027 m/m and a typical concave longitudinal profile (Figure 14) as measured from 1:24,000 scale USGS topographic quadrangle maps. While basin slope and concavity are generally dependant upon sediment load, sediment size, and discharge, lithology is also an important control in some areas (Knighton, 1998). The basin slope for Wilson Creek may be substantially influenced by bedrock. Outcrops within the channel bed were observed at many sampling locations and the basin slope is in accord with those found by Brush (1961) for basins of similar length having limestone bedrock. Bedrock controlled

areas may be responsible for reach-scale deviations from a smooth concave profile as seen at site 27 and in the headwater reaches upstream of site 37 (Figure 14). Sediment bound pollutant transport and storage can vary due to these localized changes in slope, departing from the idealized process model of erosion in the upper stream reaches, transport in the middle reaches, and deposition in the lower watershed reaches (Schumm, 1977).

Channel Cross-section Surveys. Channel cross-section surveys were conducted at each of the nine overbank sites (Figures 8 & 14) with the results graphed in Figure 15. Cross-sectional area (CSA) was calculated as the product of measured channel width and average depth at the bankfull and low terrace heights and is reported in Table 10. Generally, bankfull CSA measures ranged between 5 m² and 8 m² at most sites with the

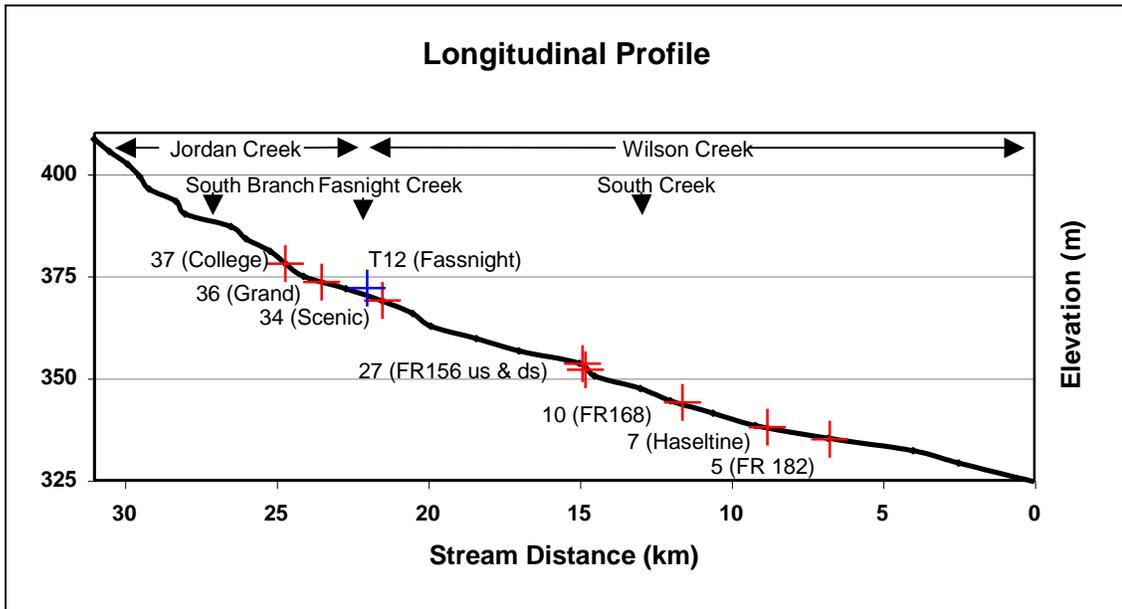


Figure 14. Longitudinal profile of the Wilson Creek watershed showing overbank sampling sites.

two lower sites measuring more than 14 m². Total channel cross-sectional area, measured at the low terrace height, typically increases downstream with increasing drainage area and discharge (Knighton, 1998). This relationship was not consistently observed at the surveyed sites, but instead CSA values were highly variable. The two most upstream sites, 36 and 37, had larger CSA measures than did site 5 in the lower watershed which has the largest drainage area. Urbanization in the upper watershed, with impervious surfaces and storm sewer-stream connections, is likely responsible for the enlarged channels at upstream locations. The channels in the upper watershed are not necessarily incised relative to lower watershed sites, as revealed by surprisingly high width : depth ratios at sites 37, 19, and 27_{us} (Table 10). Karst features such as springs, sinkholes, estevelles, and losing and gaining stream reaches also contribute to the hydrologic complexity and channel geometry abnormalities.

Table 10. Channel geometry at overbank sites.

Site # (name)	Width (m)		Depth (m)		CSA (m ²)		Width / Depth	
	Bf	Ttl	Bf	Ttl	Bf	Ttl	Bf	Ttl
T12 (Fassnight)	8.6	12.8	0.57	1.45	4.9	18.6	15.1	8.8
37 (College)	14.3	28.9	0.35	1.10	4.9	31.8	40.9	26.3
36 (Grand)	12.4	23.3	0.68	1.50	8.5	35.0	18.2	15.5
34 (Scenic)	9.7	22.8	0.47	1.15	4.6	26.2	20.6	19.8
27 (FR156 us)	14.6	20.8	0.37	1.04	5.3	21.6	39.5	20.0
27 (FR156 ds)	10.2	12.9	0.47	1.41	4.7	18.2	21.7	9.1
27 (FR156 avg)	12.4	16.9	0.42	1.23	5.2	20.6	29.5	13.8
10 (FR168)	13.9	15.8	0.48	1.25	6.7	19.8	29.0	12.6
7 (Haseltine)	21.1	25.7	1.04	1.80	21.9	46.3	20.3	14.3
5 (FR182)	23.9	26.7	0.63	1.12	14.9	29.9	37.9	23.8

Bf -Bankfull channel

Ttl -Total channel (low terrace surface)

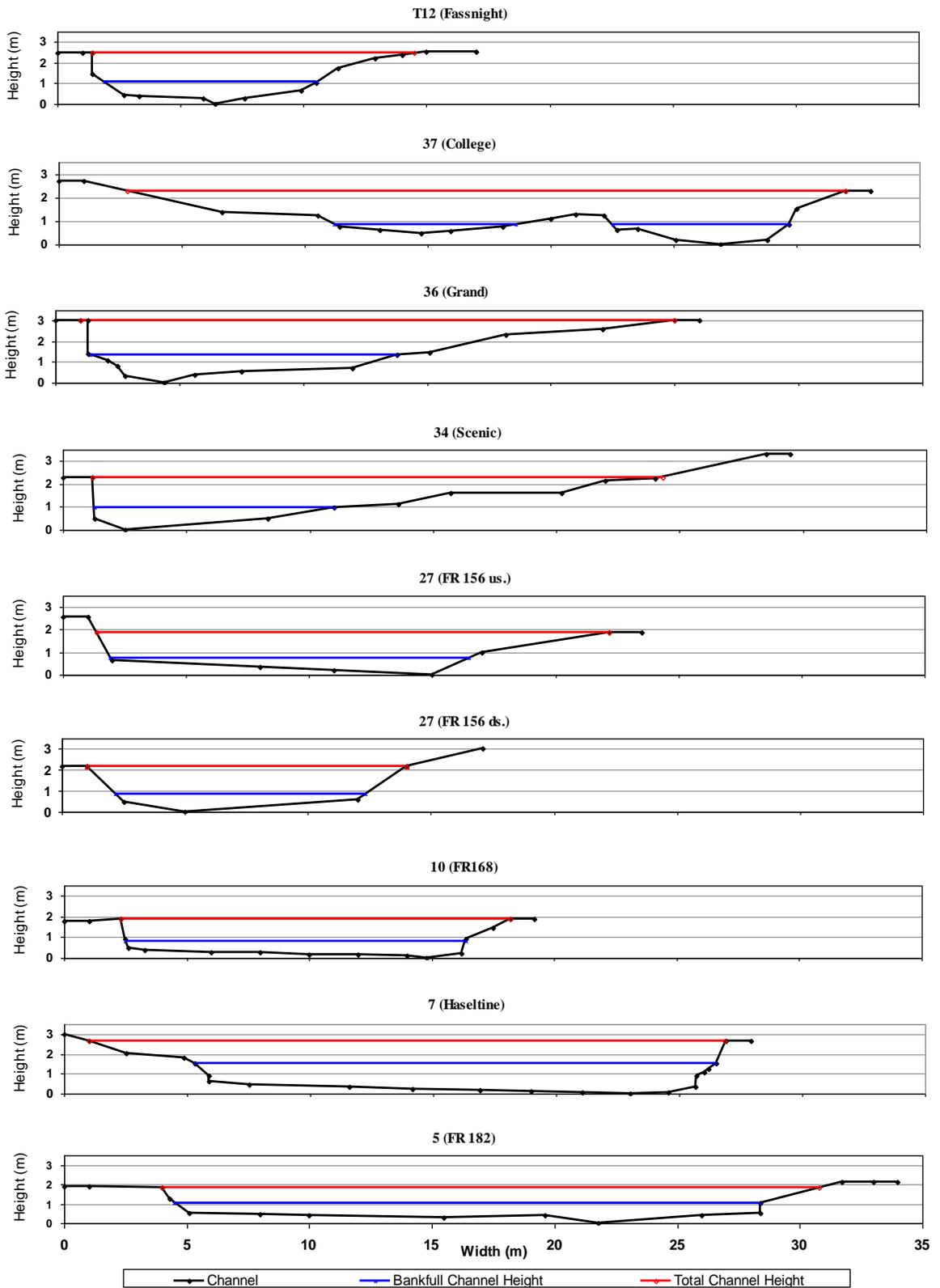


Figure 15. Channel cross-sections with bankfull and total channel stages

Channel Capacity. Bankfull discharge and total channel capacity at the low terrace stage were estimated using the continuity equation:

$$Q = CSA * V$$

Where Q is the estimated discharge in cubic meters per second (cms), CSA is the measured cross-sectional area in square meters, and V is the stream flow velocity in meters per second (m/s).

Velocity was estimated using the Manning equation:

$$V = (C * R^{0.66} * S^{0.5}) / n$$

Where C is a conversion constant equal to one for meter units, R is the hydraulic radius of the channel estimated by $(W * D) / (2D + W)$, and S is the channel slope at the sample site. The variable, n, is Manning's roughness coefficient set at 0.04 and 0.035 for bankfull and total channel calculations, respectively. These n values were selected based upon the knowledge and field measurements of previous investigators at nearby streams (Pavlowsky, 2004). Estimates of bankfull and total channel capacity discharges at each overbank site are reported in Table 11. These discharges do not uniformly increase downstream owing to the variability in CSA at the sampled sites.

Table 11. Bankfull and total channel capacity discharges.

Site # (name)	CSA (m ²)		R (m)		S (m/m)		V (m/s)		Q (cms)	
	Bf	Ttl	Bf	Ttl	Bf	Ttl	Bf	Ttl	Bf	Ttl
T12 (Fassnight)	4.9	18.6	0.51	1.18	0.0022	0.0022	0.75	1.31	3.7	24.4
37 (College)	4.9	31.8	0.33	1.02	0.0055	0.0055	0.90	1.88	4.4	59.8
36 (Grand)	8.5	35.0	0.62	1.33	0.0022	0.0022	0.85	1.41	7.2	49.4
34 (Scenic)	4.6	26.2	0.43	1.04	0.0028	0.0028	0.76	1.36	3.5	35.7
27 (FR156 us)	5.3	21.6	0.35	0.95	0.0061	0.0061	0.97	1.88	5.2	40.7
27 (FR156 ds)	4.7	18.2	0.43	1.16	0.0061	0.0061	1.11	2.15	5.3	39.1
27 (FR156 avg)	5.2	20.6	0.39	1.05	0.0061	0.0061	1.04	2.02	5.4	41.7
10 (FR168)	6.7	19.8	0.45	1.08	0.0022	0.0022	0.69	1.23	4.7	24.4
7 (Haseltine)	21.9	46.3	0.94	1.58	0.0013	0.0013	0.87	1.22	19.0	56.4
5 (FR182)	14.9	29.9	0.59	1.03	0.0011	0.0011	0.59	0.85	8.8	25.3

Two-year Flood. The two-year flood at each site was estimated using a USGS (1995b) regional regression equation:

$$Q_2 = 77.9 Ad^{0.733} * S^{0.265}$$

Where Q_2 is the estimated two-year flood, Ad is the upstream drainage area in square miles, and S is the basin slope in feet per mile. The estimated two-year flood discharge for each overbank site is shown in Table 12. Drainage area at each overbank site was calculated using the spatial analysis features in ArcMap 9.0 and is shown in Figure 16. Although the regional regression equation used to estimate the two-year flood discharge was developed from rural stream data, its use is appropriate here to highlight the channel capacity differences between the urbanized upper watershed and the more rural land uses in the lower.

Table 12. Upstream drainage area at overbank sites and estimated two-year discharge.

Site # (name)	Ad		S _{basin}		Q _{2yr}	
	mi ²	km ²	ft/mi	m/m	cfs	cms
T12 (Fassnight)	4.6	11.9	14.2	0.0027	481.2	16.9
37 (College)	12.1	31.4	14.2	0.0027	979.9	34.6
36 (Grand)	13.2	34.2	14.2	0.0027	1043.2	36.8
34 (Scenic)	19.0	49.2	14.2	0.0027	1361.9	48.1
27 (FR156 us)	36.4	94.4	14.2	0.0027	2195.8	77.5
27 (FR156 ds)	36.4	94.4	14.2	0.0027	2195.8	77.5
10 (FR168)	50.8	131.5	14.2	0.0027	2799.7	98.9
7 (Haseltine)	54.7	141.7	14.2	0.0027	2957.3	104.4
5 (FR182)	58.3	150.9	14.2	0.0027	3096.9	109.4

* USGS (1995b) Regional Regression Equation $Q_{2yr} = 77.9 * Ad^{0.733} * S^{0.265}$

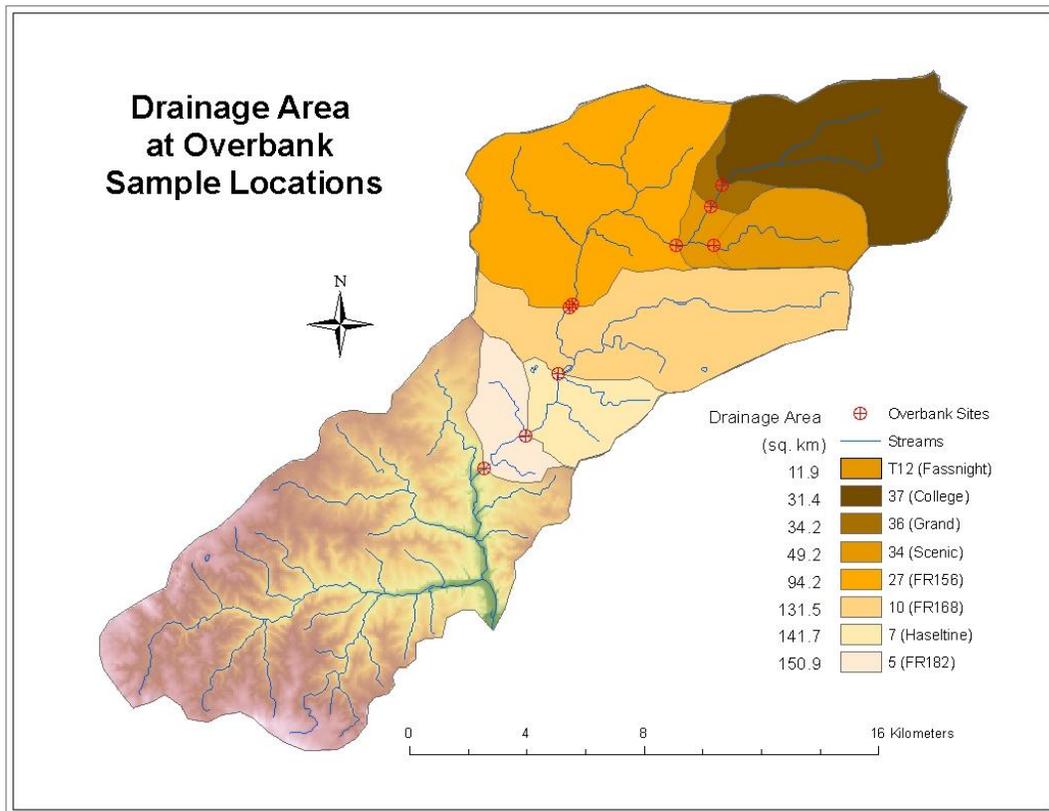


Figure 16. Drainage area at sampled overbank sites.

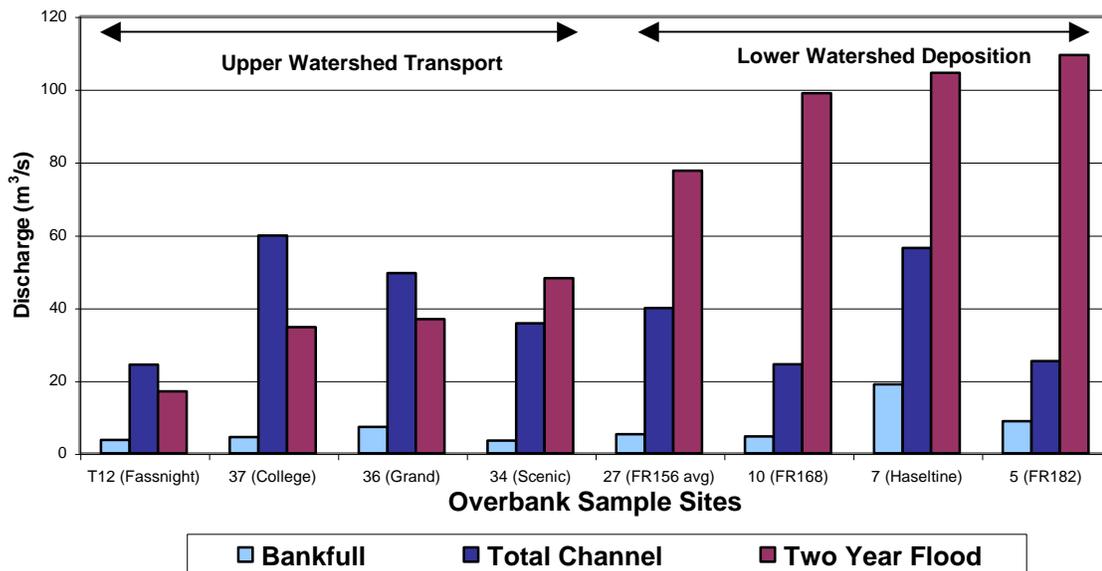


Figure 17. Total channel capacity and the estimated two year flood discharge.

The estimated two-year flood discharge at each site was converted to cubic meters per second (cms) and graphically compared to bankfull and total channel capacity at each site in Figure 17. While the two-year flood exceeds bankfull capacity at all sites, the enlarged total channels in the upper watershed completely contain estimated two-year flood discharges at nearly every site. Low terrace surfaces at surveyed channels at site 27 and below, however, are exceeded during two-year flows by a wide margin. This channel geometry-related difference in upper and lower watershed hydrology is due to the spatial difference in human impact upon the watershed during historical times. The upper watershed urbanization has enhanced the natural tendency for sediment erosion and transportation in the upper stream reaches since larger floods are contained by the channel and there are fewer opportunities for overbank deposition. The enlarged channels in the upper watershed quickly convey floodwater and sediment-bound mercury to the lower watershed. Channelization and bank stabilization measures upstream of site

37 have served to retard, and to some extent arrest, the erosion of bank sediment from these reaches. This has promoted channel enlargement at the upstream survey sites 37 and 36 located just downstream of bank and bed stabilization structures.

The upper and lower watershed differences in the channel's capacity to convey the two-year flood, as illustrated in Figure 17, affect sediment erosion, transport, and storage. This human impact to the fluvial system will also affect the distribution of sediment bound pollutants, such as mercury, released during historical times. Therefore, the sediment data collected within the watershed has been divided into two subsets for geochemical and spatial analysis. This division is made just upstream of site 27 as seen in Figure 8. The lower watershed will include sites 1 through 27, T1 through T10, and S1 through S4. The upper watershed sites include sites 28 through 42, T11 through T16, and S5 through S8.

Sediment Characterization

Sediment Texture and Data Normalization. Grain size was measured on a small subset of sediment samples consisting of nine channel samples, nine post-settlement overbank samples, and nine pre-settlement samples. The mean percentages of sand, silt, and clay, determined by the hydrometer method, are shown in Table 13. Channel sediment was relatively coarse with sand-silt-clay distribution nearly equal. The overbank sediment was generally half silt and a third clay, basically the composition of a silty clay loam soil. These findings are consistent with the upward fining expected in the fluvial environment as a result of hydraulic sorting (Knighton, 1998). The silty texture of overbank sediments was also found by Shade (2003) in multiple core samples extracted

Table 13. Percent Sand (> 63 μm) – Silt (63 μm > x > 2 μm) – Clay (< 2 μm) fraction^a in Channel, Post-settlement, and Pre-settlement deposits.

	Channel (n = 9 ^b)			Post-Settlement (n = 9 ^b)			Pre-Settlement (n=9 ^b)		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
Mean	36	35	29	18	50	31	10	54	36
St. Dev.	30	17	16	17	14	6	14	18	12
CV %	82	48	56	94	29	19	136	34	33

^a Particle size determination using hydrometer method (Gee and Bauder, 1986)

^b Subset is not necessarily a random sample of the entire data set.

from the flood plain in the lower watershed. Percent sand is highly variable, having a CV value greater than 100 %, in the typically silty pre-settlement overbank sediment due to the presence of coarser buried lateral accretion deposits at some sites.

The samples of the subset analyzed were not randomly selected to represent the entire data set. Instead, samples were chosen according to aluminum content to assess the use of aluminum to normalize for any grain size effect in mercury accumulation. Aluminum normalization is common in sediment studies (Piper, 1971; Din, 1992) because it is thought to have uniform flux from crustal-rock sources, from the time sediment particles were eroded until the time they were deposited (Horowitz, 1991). In addition, aluminum is part of the crystal structure of aluminosilicate clay minerals that make up a significant portion of the fine-grained sediment fraction.

The percent clay fraction was strongly correlated with aluminum percent (Figure 18). The three depositional environments had similar distributions with clay fraction – aluminum association being strongest in channel sediment ($R^2 = 0.81$), slightly weaker in pre-settlement overbank deposits ($R^2 = 0.70$), and markedly weaker in the post-settlement overbank deposits ($R^2 = 0.49$). The weaker association in the post settlement deposits was likely due to the narrower range of aluminum content in this subset (0.5 % – 2 %).

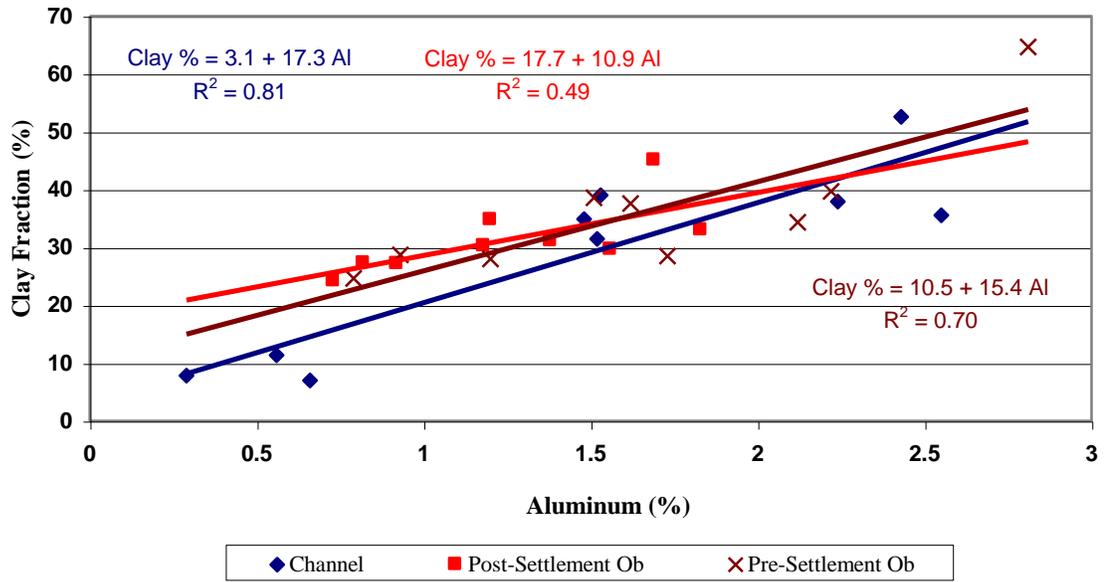


Figure 18. Percent clay fraction to percent aluminum for three depositional environments.

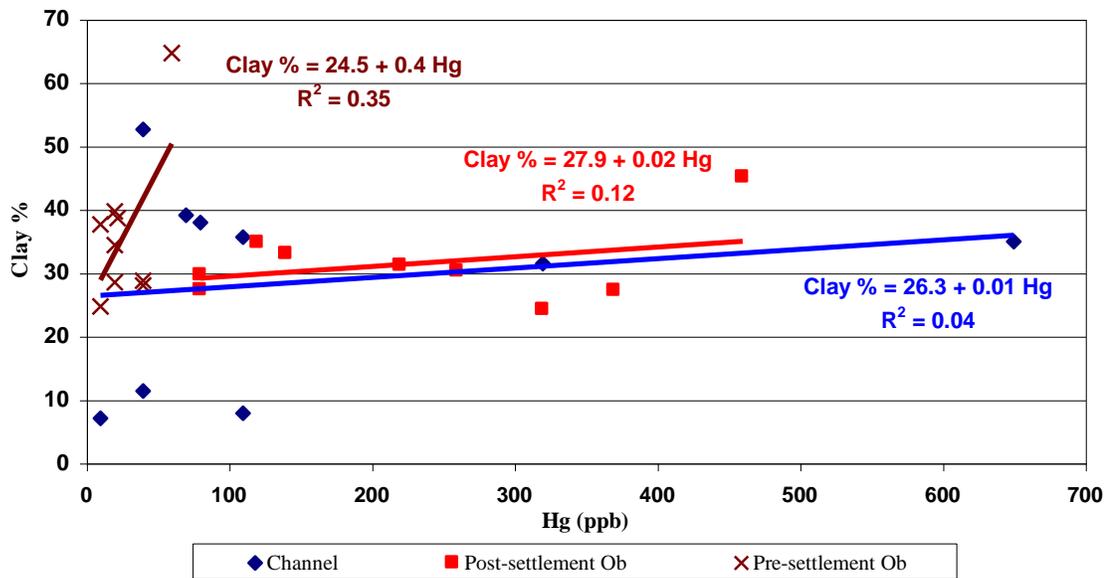


Figure 19. Percent clay fraction to mercury (ppb) for three depositional environments.

The next step in determining the appropriateness of aluminum normalization to aid in the assessment of mercury distribution was to evaluate the relationship between the clay percent and mercury content of the selected sediment samples. The plot comparing clay fraction to mercury is shown in Figure 19. Mercury and clay content in the sediment samples analyzed were poorly related. Data trendlines for the three sediment types had low R^2 values. Pre-settlement deposits showed a slightly higher association ($R^2 = 0.35$) possibly due to natural accumulation or background concentration prior to anthropogenic mercury sources to the system. Yet, the plot suggests that the trendline may be influenced by an outlier, thus yielding little information about mercury adsorption due to clay sized particles. Richardson et al. (2002) also found little association between mercury and grain size in contaminated sediment downstream of an industrial mercury source. While grain size is widely recognized as an important accumulation factor for mercury (Horowitz, 1991), it may be possible that anthropogenic inputs disrupt the natural concentration trends due to grain-size sorption relationships alone. Contamination affects are found across all size distributions and are at a much higher level, thus overwhelming the background signal and masking mercury grain-size trends. In addition, groundwater flows and redox changes may cloud grain-size – mercury correlations in the pre-settlement deposits since they are closer to the channel water table.

The poor mercury – clay association seen in Figure 19 does not support the use of aluminum normalization for this data set. Even though clay percent and aluminum percent are strongly related, little would be gained by normalizing for a mercury – clay relationship that is not verifiable. In addition, the failure of aluminum normalization to reduce variability in four pollutants assessed in the Error Analysis section (Table 9)

suggests that normalization may actually introduce variability leading to erroneous mercury distribution interpretations. Van der Weijden (2002) discouraged the unsubstantiated use of data normalization because it may promote: (1) spurious correlations, especially damaging when linear regression techniques are applied; (2) masked enrichment or dilution processes, whereby explanatory distribution factors are veiled by the altered data; and (3) loss of information, harmful when the pollutant's concentration is relevant. Although aluminum will be investigated as a geochemical substrate in the sediment geochemistry section, in light of these considerations aluminum normalization will not be employed to examine mercury distribution.

Organic Matter Content. The determination of organic matter content in the sediment samples collected is for this study is important because of its role as a geochemical substrate and as an indicator of buried soils in the overbank deposits within the watershed. A summary of organic matter content can be seen in Table 14. Mean organic matter percent was higher and more variable in the channel sediment than in the overbank deposits. This may be due to multiple sources and seasonal distribution of OM inputs to the channel environment. Sources such as leaf litter from aquatic plants and forested riparian corridors in the middle and lower watershed, yard waste delivered to the stream via storm sewers in the upper watershed, and animal waste from wildlife. Organic matter content in both pre- and post-settlement Overbank deposits were similar with post-settlement sediment having a slightly higher mean percentage and higher variability. This is possibly due to high organic content in the top few centimeters of developing soils at the floodplain surface. These sediments are actively processing organic inputs from plants and animals.

Table 14. Percent organic matter (LOI) in the three depositional environments.

	Channel (n = 135) ^a	Post-Settlement (n = 63) ^b	Pre-Settlement (n=57) ^c
Mean	9.6	6.6	5.0
St. Dev.	3.7	1.8	0.9
CV %	38.7	27.7	17.2

^a Channel deposits include low flow and bankfull samples from the main channel and tributary sites

^b Overbank deposits greater than or equal to 50 ppb Hg.

^c Overbank deposits less than 50 ppb Hg.

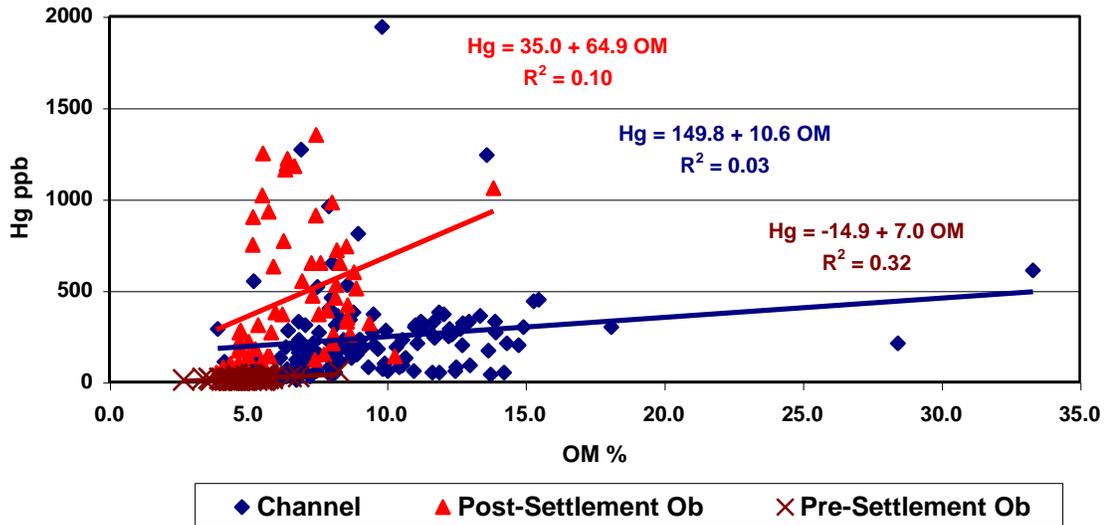


Figure 20. Mercury concentration to Organic Matter for each depositional environment.

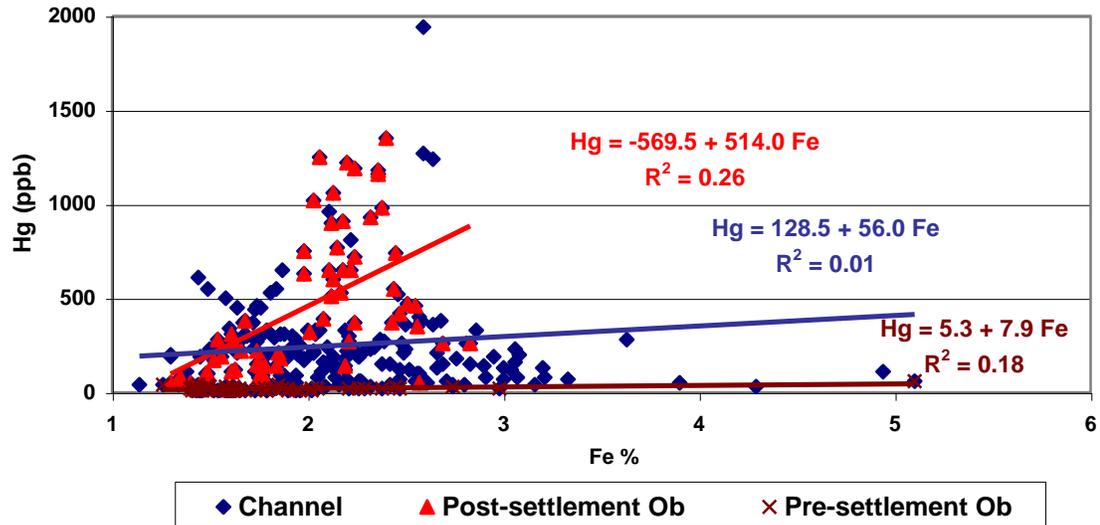


Figure 21. Mercury concentrations to iron for each depositional environment.

Organic matter and iron percent were plotted against mercury concentration in channel and overbank deposits and shown in Figures 20 and 21, respectively. Disregarding deposit type, both organic matter and iron are distributed similarly when plotted against mercury. Low mercury levels are found in sediments of widely varying organic matter and iron content. The range of organic and iron content in the sediment decreases at higher levels of mercury content. This effect highlights the presence of different deposit types with differing substrate associations. Organic matter has a slightly tighter grouping within each of the three different sediment types than that displayed by iron. Although possibly influenced by outliers, stronger associations with mercury exist for organic matter in channel deposits and in post-settlement overbank deposits for iron. Mercury association with iron in the contaminated historical sediment may relate to the smaller grain-sizes in these overbank deposits, while organic matter associations in channel sediment may be due to organic inputs as discussed above.

In general, OM percent for channel samples ranged from 5 to 15 percent at mercury concentrations below 500 ppb. Post-settlement overbank deposits were generally lower in OM, between 5 to 10 percent, and higher in mercury with concentrations up to 1500 ppb. Both OM and mercury were lower in pre-settlement samples with OM generally between 2.5 and 8 percent while mercury was mostly below 20 ppb, with all values for pre-settlement constrained to below 50 ppb by definition. These clear groupings of organic matter and mercury concentrations serve to verify the unique identity of the three depositional environments. The existence of both geochemical and obvious spatial

divisions between these sediment types support the use of separated analysis, description, interpretation of mercury distribution.

The distribution of organic matter in selected overbank deposits are shown in Figure 22. The six overbank profiles were selected because a buried A soil horizon (Ab) was visible at each of these cutbank sites during sample collection. The buried soil was typically observed as a horizontal band of darker color and coarser texture than overlying sediment as seen in Figure 23. The small trowel with orange flagging tape tied to the handle marks the top of the buried A horizon. The horizontal red line at each site in Figure 22 represents the depth of the buried soil at that site.

In general, organic matter was high, typically between 8 and 10 percent, in the A horizon of the floodplain surface; decreasing with depth to below five percent. Previous investigations have reported similar findings (Shade, 2003). Increases or abrupt variations in organic content near the buried soil depth are plotted for the upper watershed sites T12, 34, and 36, in Figure 22, while relatively little change is observed at Ab depths in the lower watershed profiles. This may indicate abrupt sedimentation rate changes in the upper watershed and more gradual changes in the lower, facilitating increased leaching and decomposition.

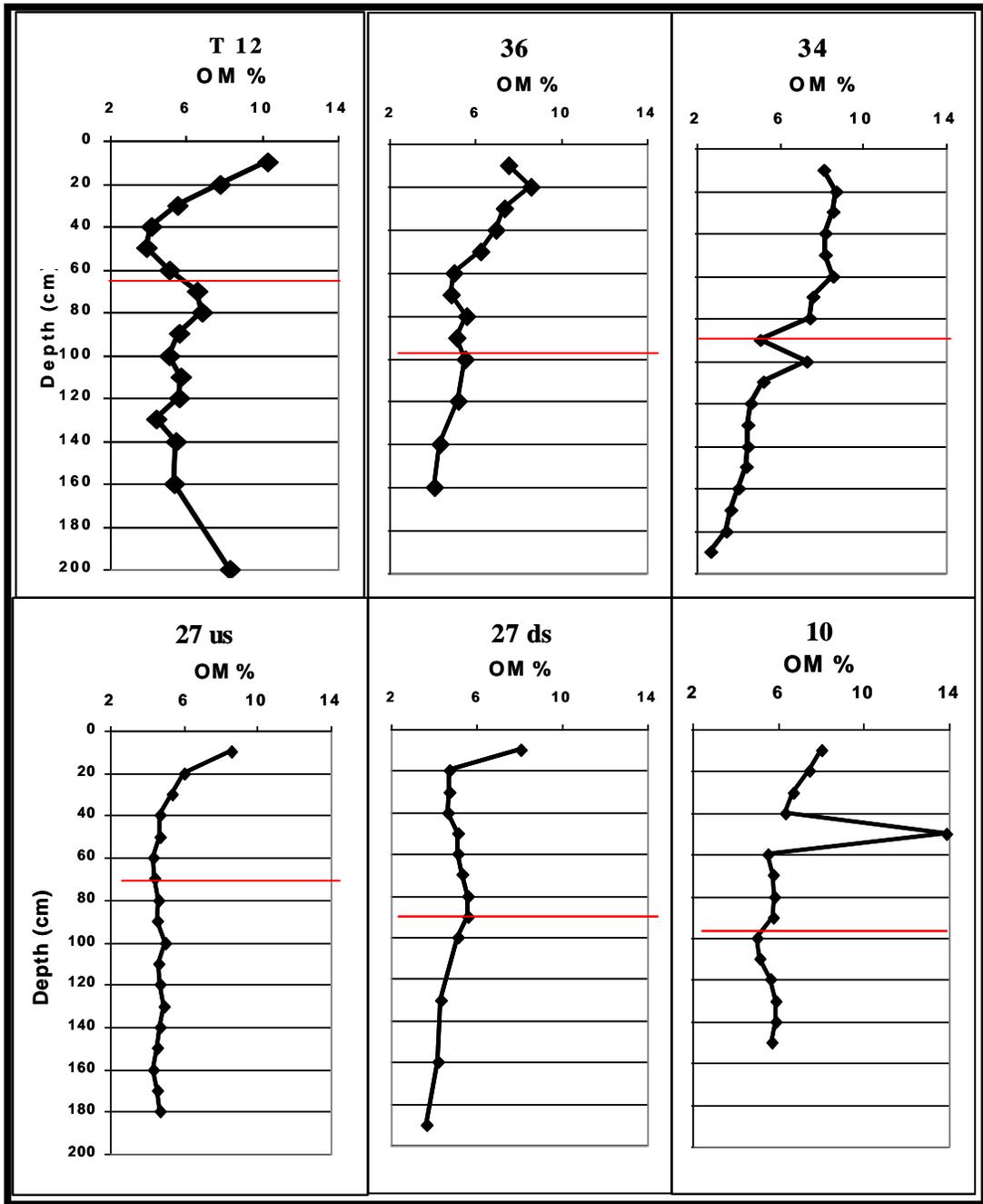


Figure 22. Overbank profile of organic matter and depth of observed buried soil in red at sites T12, 36, 34, 27 upstream, 27 downstream, and 10.

Sedimentation

Buried Soil Surface Dating. Buried soil depths were observed at several sites between 70 and 100 cm depth as shown with a red line in each profile in Figure 22. A coarse textured buried point bar deposits was noted at site 5 during sample collection at approximately 70 cm depth. Sharp visible contrast between stratigraphic layers was not observed at sites 7 and 37, possibly due to the site specific conditions of moisture content and site disturbance, respectively.



Figure 23. Buried soil in the overbank deposits at site T12 (Fassnight) at approximately 60 cm depth near orange flag on trowel.

The estimation of sedimentation rates and later discussion of the timing of historical pollution release are dependent upon the date assigned to the buried soil surface. The date of 1870 seems reasonable to assign to this surface as it occurs at the intersection of periods of watershed disturbance and industrial growth. Local land clearing activities began shortly after early settlement in the 1830's and 1840's. Widespread deforestation of the watershed probably occurred a few decades later as timber harvest accelerated to supply the growing demand for railroad ties (Rafferty, 2001). The onset of stream instability and accelerated sedimentation probably occurred between 1850 and 1880.

The arrival of the Atlantic Pacific Railroad in 1870 and others, over the next decade, boosted manufacturing operations that had previously been limited to local markets (Rafferty, 2001). Population also increased nearly four-fold from 5,555 to 21,850 between 1870 and 1890 (Shade, 2003). It is realistic to expect metal pollution to accompany this expansion in manufacturing in 1870 and to continue during industrial growth into the 1950's. Thus 1870 is common to both periods: fluvial system instability between 1850 and 1880, and railway-related manufacturing and processing expansion between 1870 and 1950.

Cesium Dating. The activity of ^{137}Cs in sediment samples collected at five overbank sites was measured by Dr. Jerry Ritchie of the USDA and is reported in Figure 24. The ^{137}Cs profiles generally peak at the floodplain surface near 15 to 30 Bq/kg and decrease to 0 Bq/kg by 40 cm depth. Peak ^{137}Cs activity at the surface indicates that little deposition on the low terrace surface has occurred since peak ^{137}Cs atmospheric fallout in 1964. Site 36 was the only site at which post-1964 sedimentation was indicated by ^{137}Cs dating. The fifteen centimeter depth of the 1964 surface would suggest an average

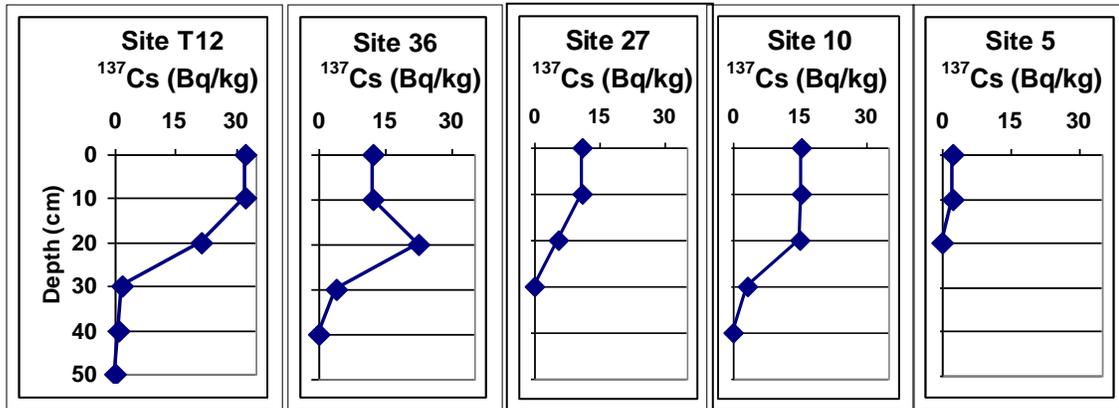


Figure 24. ¹³⁷Cesium profiles from two upper watershed sites (T12 & 36), and three lower watershed sites (27, 10, & 5).

rate of 0.38 cm/yr until 2003. Given the channel's capacity at site 36 to completely contain high discharge flow events (Figure 17) it is unlikely that alluvial deposition would account for the apparent sedimentation at this site. It is more likely that surface runoff from the nearby street intersection has accumulated colluvial sediment at this site from adjacent terrace surfaces. In addition, rate calculations for such thin deposits (15 cm) have a wide margin of error due to 10 cm depth integrated samples collection.

The ¹³⁷Cs profile at site 5 was unusual in both its low peak activity and shallow terminus. As such, it resembles the lower portion of the other profiles. This may suggest that the low terrace surface at this site is geomorphically active possibly experiencing cycles of erosion and scour in recent years. This is congruent with channel capacity findings reported earlier and with previous ¹³⁷Cs dating of floodplain deposits at 3.2 km from the James River confluence indicate that the 1964 depth was 10 cm below the 2002 surface (Shade, 2003). This apparent aggradation is more likely a result of alluvial processes at this site due to similar findings at several core samples across the low terrace surface and a more precise sampling procedure in which depth integrated samples were collected at 5 cm intervals.

Table 15. Overbank sedimentation rate estimates using Cs dating and buried soil horizon.

	T12 (Fassnight)	36 (Grand)	27 (FR 156)	10 (FR 168)	5 (FR 182)
1964 Depth (cm) (¹³⁷ Cs Peak)	0	15	0	0	0
1870? Depth (cm) (Buried Soil*)	60	70	70	95	70
Sedimentation Rates (cm/yr)	0.64	0.59	0.74	1.01	0.74

* Buried point bar deposits at site 5.

Sedimentation Rates. Sedimentation rate estimates were calculated and reported in Table 15 for two upper watershed and three lower watershed overbank sites for which ¹³⁷Cs analysis was completed. The possibility of post-deposition ¹³⁷Cs mobility due to bioturbation in soils makes the use of a 1954 date of first occurrence unreliable. Therefore, rates were calculated for historical deposits between the 1964 surface, dated by peak ¹³⁷Cs activity, and the 1870 buried soil surface. Historical sedimentation rates at the five sites ranged, in general, from one half to one centimeter per year as shown in Table 15. Rates were higher at lower watershed sites ranging from 0.74 to 1.01 cm/yr. These rates match the average sedimentation rate of 0.80 cm/yr calculated by Shade (2003) for an alluvial deposit in the lower watershed. Similar sedimentation rates were measured by Carson (1999) in the nearby Honey Creek watershed. Average sedimentation rates ranged from 0.82 cm / yr, for the time period between 1916 – 1998, to 0.60 cm / yr between 1896 – 1916.

SEDIMENT-MERCURY GEOCHEMISTRY

Watershed Trends

Mercury concentrations in all samples ranged from 10 to 1940 ppb. Mean mercury concentrations with each associated coefficient of variation and minimum, maximum, and mean mercury concentrations are compared by depositional environment and by watershed location in Figure 25 and Tables 16 and 17. Although the highest maximum level was found in active channel sediment, mean concentrations in the contaminated, or post-settlement, overbank deposits were nearly twice as high as mean mercury levels in channel deposits. Mean mercury concentrations were higher in the lower watershed samples for all but the uncontaminated, or pre-settlement, overbank deposits.

Channel Sediment Contamination

Channel samples were collected from depositional environments at the bankfull surface and low flow areas near the channel edge or bed. Mercury measured in sediment from these channel landforms ranged from as little as 10 ppb to as much as 1940 ppb. Summarized mercury data are reported in Table 16 according to the channel landform sampled and upper or lower watershed location. Figure 26 graphically depicts the same data. Sediment collected from channel edge and bankfull deposits had consistently higher mercury concentrations than bed sediment. The increase in mercury concentration with increasing height above the thalweg within the upper watershed samples, as seen in Figure 26, may result from upward fining and increased mercury adsorption to substrates in the fine-grained fraction. The weaker expression of the same pattern at lower watershed sites may indicate that increased mercury delivery to the streams has

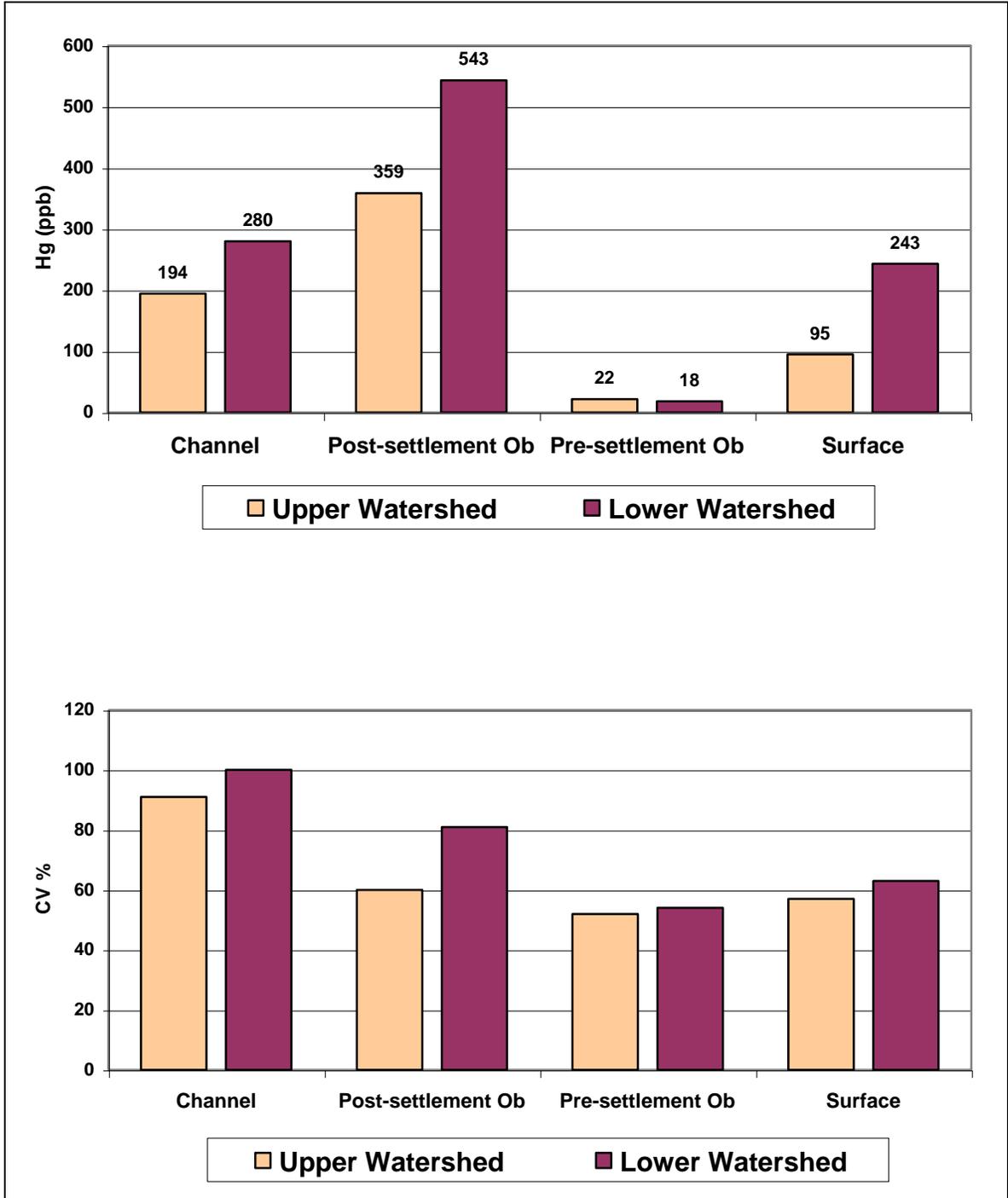


Figure 25. Mean sediment mercury concentrations and coefficient of variation (CV) by deposit type and watershed location.

Table 16. Sediment mercury concentration (ppb) from different channel landforms.

	Channel Bed	Channel Edge	Bankfull Surface
Upper Watershed	n = 3	n = 27	n = 25
Min.	60	30	30
Max.	190	380	1240
Mean	117	151	249
Lower Watershed	n = 23	n = 35	n = 22
Min.	30	50	10
Max.	810	1940	650
Mean	207	318	296

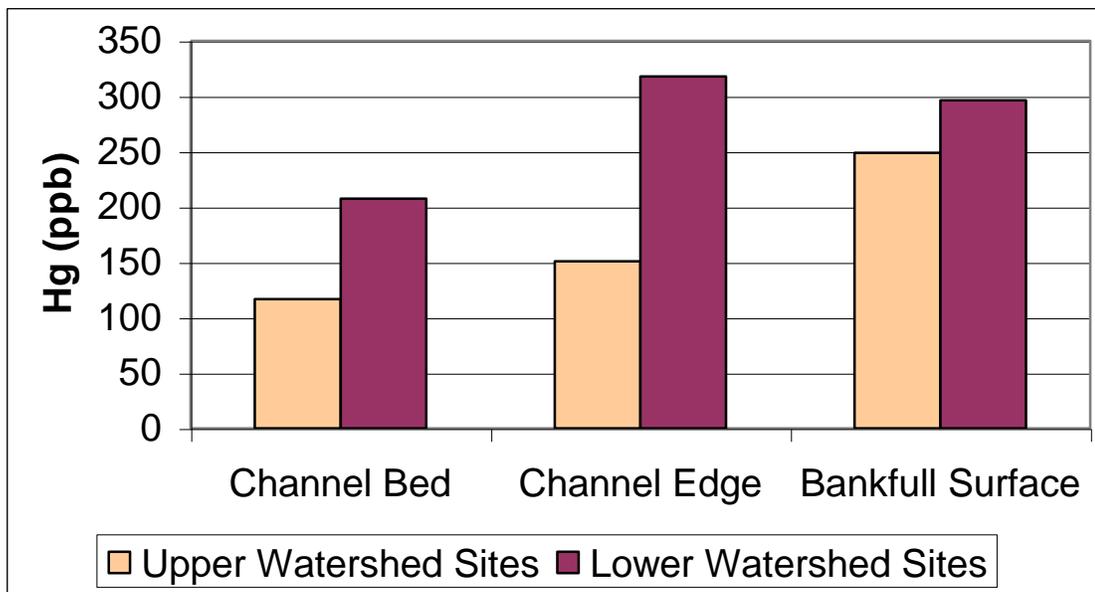


Figure 26. Mean mercury concentration by channel landform and location

overwhelmed the natural adsorption processes. Lower watershed deposits had higher mercury concentrations than upper watershed sites for all three landforms sampled. Higher mercury concentrations in the active channel sediment at the downstream locations may indicate lower watershed mercury sources to the stream environment.

Overbank Deposit Contamination

Overbank Sediment mercury profiles are plotted for each of the nine overbank sites in Figure 27. Peak mercury concentrations occur deeper in the profile at the main channel upper watershed sites 37 (40 – 45 cm), 36 (30 – 40 cm), 34 (50 – 60 cm). The lower watershed sites have much shallower peak mercury depths ranging from 0 to 30 cm. This indicates earlier contamination at locations closer to the upstream historical industrial sources. Channel incision and enlargement, channelization and bank stabilization structures, and the installation of storm sewer network in the urbanized portions of the upper watershed during the last century has greatly reduced the sediment supply to overbank environments in these areas. The sedimentation focus was therefore shifted downstream as the upper watershed became increasingly dominated by transport processes. The lower watershed reaches continued to receive contaminated sediment after upstream floodplain surfaces had been abandoned. Similar downstream sedimentation focus migration was reported by Leece and Pavlowsky (2001) due to mining-related contamination and watershed disturbance sequences.

The overbank mercury profiles in Figure 27 also show that the three down stream reaches, sites 5, 7, & 10, have mercury concentrations approximately two times higher than those found at upstream sites. Even sites 27 upstream and downstream, whose low terrace surfaces have been shown to be inundated by the two year flood, have much lower

mercury concentrations than the three sites further downstream. This suggests that contamination at sites 5, 7, & 10 is not only from more recent sources, but also from sources below site 27.

Buried soil surfaces observed at several sites correspond well to the depths of initial mercury contamination (Figure 27). This suggests that increased sediment supply from land clearing and timber harvest activities was concurrent with industrial waste discharges to Jordan and Wilson Creeks. The onset of mercury contamination in the historical post-settlement deposits was slightly above the depths of the observed buried soil. Exceptions are site 27 ds which has approximately 40 cm of uncontaminated sediment above the Ab depth and site 34 which has elevated mercury concentrations extending 10 cm below the buried soil depth. Variations in floodplain topography may account for early deposition of uncontaminated sediment at site 27 downstream as its pre-settlement surface was approximately 20 cm lower than that observed at site 27 upstream. Elevated mercury at 10 cm below the buried soil depth at site 34 may have resulted from bioturbation on the floodplain surface during the early stages of settlement-related sedimentation.

Identification of Pre-settlement Overbank Deposits. In light of the small discrepancies noted above, and the fact that buried soils were not observed at all sites, the exact buried soil depth was not used to differentiate between pre- and post-settlement overbank deposits. Instead, the mercury concentration of 50 ppb was employed as a geochemical boundary marker. Contaminated overbank deposits were considered post-settlement until the depth at which concentrations dropped below 50 ppb. Pre-settlement deposits are those below that 50 ppb depth. For most sites the 50 ppb depth corresponds to the buried soil depth. Sediment mercury concentrations deep in the pre-settlement profile that exceed 50 ppb, such as at sites T12 and 5, are still considered pre-settlement deposits because they were beneath the 50 ppb cut off near the buried soil.

Background Mercury Levels. Background mercury levels were determined by calculating the average mercury concentration of the pre-settlement overbank deposits. The average of both upper and lower watershed pre-settlement deposits was 20 ppb. This represents the mercury concentration found in Wilson Creek sediment before the onset of anthropogenic metal pollution. This background concentration is due primarily to the natural processes of weathering and erosion from local geologic sources and subsequent transport, sorting, and deposition on the pre-settlement floodplain.

These pre-settlement deposits are expected to represent regional background levels and will serve as a gage whereby to quantify the enrichment of mercury in upper overbank and channel sediment deposits. This concentration is very close to background levels of 18 ppb determined by Shade (2003) below buried soil depths at a the lower watershed location.

Mercury – Substrate Associations

The distribution of mercury in stream sediments is influenced by the various substrate surfaces upon which it can adsorb (Horowitz, 1989; 1991; Gabriel and Williamson, 2004). The concentrations of Organic matter, and the elements aluminum (Al), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), and sulfur (S) were evaluated to aid in mercury distribution interpretation and source identification. Minimum, maximum, and mean concentrations for these substances are reported in Table 17. Correlation matrices are shown in Tables 18 and 19 and regression models in Table 20. The data were divided into subsets by deposit type: active channel, post-settlement overbank, pre-settlement overbank, and watershed surface; and by upper or lower watershed location.

Pearson correlation and multiple regression analysis were used to assess the association between sediment bound mercury and selected geochemical substrate elements and organic matter. Pearson correlation analysis is useful for examining the association between two variables through the coefficient of correlation. Multiple regression is useful in sediment studies to determine trace metal associations (Rose et al., 1970; Horowitz, 1989). The backward stepwise procedure is used here to evaluate the strength of mercury / substrate association among multiple independent substrate indicator elements. This procedure is typically employed during the early phases of model building to select from a multitude of predictor variables the few that sufficiently reduce variability in the response variable (Kutner, 2004). While mercury concentration predictions are not the objective of this study, the backward stepwise procedure is well suited for selecting substrates according to their relationship to mercury concentration. This information may illuminate distribution patterns and aid in source identification.

Table 17. Sediment geochemistry summary for mercury and substrate elements in active channel, overbank, and watershed surface deposits in the upper and lower watershed.

Sample Type		Hg ppb	OM %	Al %	Ca ^a %	Fe %	Mg %	Mn ppm	S ^b %
Channel Sediment									
Upper watershed (n = 56)	Min.	30	4.44	0.29	0.76	1.38	0.11	386	< 0.01
	Max.	1240	18.11	2.55	18.20	4.94	0.61	4430	0.15
	Mean	194	9.40	1.29	8.28	2.54	0.21	1832	0.06
Lower watershed (n = 80)	Min.	10	3.92	0.60	0.57	1.30	0.06	435	0.00
	Max.	1940	33.31	2.45	16.00	3.63	0.53	5960	0.33
	Mean	280	9.81	1.57	4.04	2.09	0.16	1866	0.07
Post-Settlement Overbank Deposits									
Upper watershed (n = 27)	Min.	50	3.87	0.73	0.31	1.30	0.06	779	0.01
	Max.	740	10.30	1.69	10.90	2.83	0.17	2560	0.06
	Mean	359	7.37	1.04	3.73	2.09	0.11	1334	0.03
Lower watershed (n = 36)	Min.	50	4.37	1.08	0.33	1.40	0.08	692	0.01
	Max.	1350	13.86	1.90	1.98	2.57	0.14	2680	0.04
	Mean	543	6.05	1.43	0.67	1.96	0.12	1489	0.02
Pre-Settlement Overbank Deposits									
Upper watershed (n = 26)	Min.	10	2.69	0.79	0.35	1.26	0.04	95	< 0.01
	Max.	60	8.26	2.81	0.59	5.10	0.16	5530	0.02
	Mean	22	5.03	1.39	0.49	1.83	0.10	880	0.004
Lower watershed (n = 31)	Min.	10	3.68	1.15	0.36	1.41	0.09	950	0.00
	Max.	40	5.89	2.26	0.46	2.74	0.17	3000	0.02
	Mean	18	4.94	1.58	0.41	1.81	0.12	1368	0.01
Surface^c Sediment									
Upper watershed (Indus. n = 4)	Min.	40	5.88	0.31	11.55	1.14	0.19	310	< 0.01
	Max.	170	12.30	1.56	26.00	2.05	0.43	1340	0.15
	Mean	95	9.43	0.81	18.11	1.73	0.31	733	0.05
Lower watershed (SWPS n = 4)	Min.	90	9.56	0.77	0.40	1.30	0.07	818	0.04
	Max.	450	14.53	1.33	1.40	1.88	0.10	1730	0.06
	Mean	243	11.15	1.05	0.74	1.59	0.08	1205	0.05

^aCalcium values above detection limits were calculated at 1 plus the detection limit (eg. >15.0 = 16.0) (n = 5)

^bSulfur values below detection limit were reported as zero (eg. < 0.01 = 0) (n = 10)

^c Upper watershed surface deposits are from the industrial area and the lower watershed deposits are from near the power plant.

Indus. – Industrial area

SWPS – Southwest Power Station

Table 18. Pearson correlations for upper watershed mercury and geochemical substrates.

Upper Watershed	Hg	OM	Al	Ca	Fe	Mg	Mn	S
Channel Sediment (n = 56)								
Hg	1.000							
OM	*0.338	1.000						
Al	0.124	0.246	1.000					
Ca	-0.228	0.033	*-0.667	1.000				
Fe	-0.097	-0.118	*0.454	-0.186	1.000			
Mg	-0.128	0.123	-0.270	*0.635	-0.187	1.000		
Mn	0.133	0.183	*0.350	-0.294	*0.702	*-0.405	1.000	
S	0.233	0.596	-0.034	0.106	*-0.341	0.041	-0.034	1.000
Post-settlement Overbank Deposits (n = 27)								
Hg	1.000							
OM	*0.506	1.000						
Al	0.258	0.149	1.000					
Ca	0.268	*0.594	-0.429	1.000				
Fe	*0.622	*0.650	0.383	0.386	1.000			
Mg	0.382	*0.756	-0.217	*0.913	*0.572	1.000		
Mn	0.062	*0.476	0.116	*0.479	*0.697	*0.482	1.000	
S	0.388	*0.854	0.077	*0.704	*0.748	*0.813	*0.777	1.000
Pre-settlement Overbank Deposits (n = 26)								
Hg	1.000							
OM	*0.698	1.000						
Al	0.364	*0.602	1.000					
Ca	0.188	*0.656	*0.457	1.000				
Fe	*0.530	0.429	*0.780	0.172	1.000			
Mg	-0.087	0.372	*0.679	0.386	0.221	1.000		
Mn	*0.642	*0.670	*0.773	0.394	*0.877	0.373	1.000	
S	0.381	0.434	-0.141	0.129	-0.254	-0.140	-0.066	1.000
Surface Street Sediment (n = 4)								
Hg	1.000							
OM	0.804	1.000						
Al	0.063	-0.070	1.000					
Ca	0.720	0.562	-0.626	1.000				
Fe	0.684	0.562	0.752	-0.013	1.000			
Mg	0.944	0.955	0.006	0.662	0.662	1.000		
Mn	0.070	-0.047	*1.000	-0.625	0.761	0.022	1.000	
S	-0.142	0.403	0.275	-0.454	0.263	0.158	0.301	1.000

* Statistically significant at the 0.01 level.

Bold coefficients are Statistically significant at the 0.05 level.

Table 19. Pearson correlations for lower watershed mercury and geochemical substrates.

Lower Watershed Channel Sediment (n = 80)	Hg ppb	OM %	Al %	Ca %	Fe %	Mg %	Mn ppm	S %
Hg	1.000							
OM	0.097	1.000						
Al	0.056	*0.345	1.000					
Ca	-0.065	0.056	*-0.278	1.000				
Fe	-0.043	*-0.266	*0.430	-0.088	1.000			
Mg	-0.108	0.248	0.050	*0.589	-0.140	1.000		
Mn	-0.100	-0.100	*0.486	-0.057	*0.759	-0.166	1.000	
S	*0.220	*0.513	0.228	-0.089	*-0.279	0.040	-0.148	1.000
Post-settlement Overbank Deposits (n = 36)								
Hg	1.000							
OM	*0.458	1.000						
Al	*0.422	0.220	1.000					
Ca	*0.486	*0.485	0.293	1.000				
Fe	*0.667	*0.463	*0.844	*0.522	1.000			
Mg	*0.491	0.326	*0.955	*0.434	*0.882	1.000		
Mn	0.252	0.225	*0.501	0.172	*0.720	*0.479	1.000	
S	*0.452	*0.580	0.240	*0.806	*0.519	*0.423	0.220	1.000
Pre-settlement Overbank Deposits (n = 31)								
Hg	1.000							
OM	0.354	1.000						
Al	0.263	*0.447	1.000					
Ca	-0.110	*0.702	0.101	1.000				
Fe	0.269	0.402	*0.953	0.057	1.000			
Mg	0.185	0.224	*0.933	-0.013	*0.916	1.000		
Mn	0.251	*0.595	*0.714	0.328	*0.833	*0.595	1.000	
S	0.163	*0.818	*0.441	*0.568	*0.430	0.220	*0.650	1.000
Surface Soils (n = 4)								
Hg	1.000							
OM	0.924	1.000						
Al	0.747	0.620	1.000					
Ca	-0.613	-0.273	-0.476	1.000				
Fe	-0.168	0.202	-0.096	0.879	1.000			
Mg	*0.991	0.917	0.653	-0.630	-0.206	1.000		
Mn	-0.103	-0.220	-0.617	-0.367	-0.584	0.025	1.000	
S	0.912	*0.986	0.506	-0.303	0.145	0.927	-0.060	1.000

* Statistically significant at the 0.01 level.

Bold coefficients are statistically significant at the 0.05 level.

Pearson Correlation coefficients in Table 18 and 19 and generated regression models in Table 20 provide valuable insights into geochemical substrate - mercury associations. These associations were analyzed in the following manner: (1) common relationships between substrate elements were identified using correlation coefficients, (2) these groups of related substrates were then evaluated for their association with mercury, with only the elements most strongly correlated with mercury in each group selected for the backward step-wise regression procedure, and finally (3) regression results were interpreted in conjunction with correlation coefficients to evaluate the control of geochemical substrates on the spatial distribution of mercury within deposit types and upper and lower watershed locations.

Covariance Among Geochemical Substrates. Common associations between iron and manganese, aluminum and calcium, and organic matter and sulfur were observed. Iron and manganese were strongly related in all deposit types except surface samples. Coefficient values ranged from 0.697 to 0.877 and were significant at the more stringent $p = 0.01$ level. The small number of surface samples ($n = 8$) and differences in terrestrial oxide weathering may account for the lack of relation between iron and manganese in these samples.

Calcium correlated strongly with both aluminum and magnesium. Its inverse relationship with aluminum was most strongly expressed in channel samples where increased calcium reflects the higher percentage of sand in channel sediment (Table 13) and subsequent decrease in the fine-fraction indicating aluminum content. Calcium and magnesium were significantly correlated in nearly all deposit types but especially so in channel and post-settlement overbank deposits. Perhaps the removal of carbonates from

the older pre-settlement deposits has slightly reduced the association of calcium and magnesium in these deposits.

Organic matter and sulfur are strongly correlated as indicated by their significant correlation coefficients in all but the upper watershed surface deposits. Significance at the $p = 0.01$ level was observed within channel and both overbank deposit environments in the lower watershed and only in the post-settlement deposits in the upper watershed. This strong relationship is likely due to the high sulfur content in organic matter (Horowitz, 1991). Lower watershed relationships may be more prominent owing to increases in sulfur availability due to nearby emissions from the SWPP.

Geochemical Substrate - Mercury Associations. For the two closely associated substrates, iron and manganese, iron appears to have a stronger link to mercury. Iron correlated with mercury at the $p = 0.01$ level in pre- and post-settlement overbank deposits in the upper watershed and again with the post-settlement overbank sediment in the lower watershed (Figure 28). Manganese correlated significantly with mercury only in the pre settlement deposits of the upper watershed. Iron was therefore selected for the regression analysis.

The closely related elements, calcium, magnesium, and aluminum, were generally equal in their correlation with mercury (Figure 28). In the upper watershed calcium was significantly related to mercury in channel sediment, magnesium to surface sediment, and aluminum to pre-settlement deposits. In the lower watershed all three substrate elements significantly correlated with mercury in the post-settlement deposits with magnesium related to surface deposits as well. Magnesium was selected for regression analysis along with aluminum due to its association with the clay percent in the sediment (Figure 17).

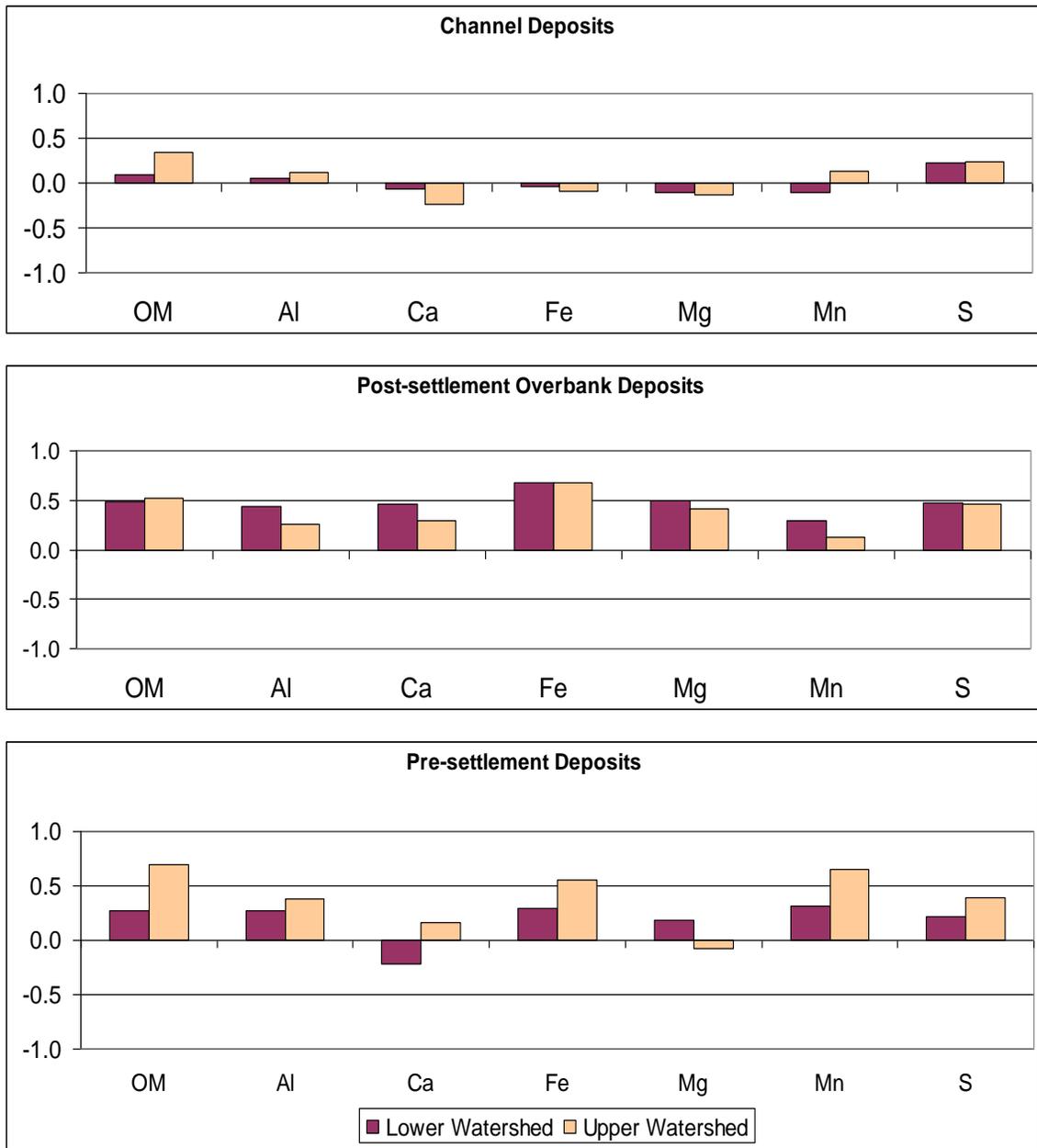


Figure 28. Correlation coefficients of geochemical substrate elements to mercury.

Organic matter was selected for regression analysis over sulfur due to its stronger association with mercury. In the upper watershed organic matter and sulfur significantly correlated with mercury in channel sediment and pre- and post-settlement overbank sediment (Figure 28). The mercury - organic matter relationship, however, was significant at the $p = 0.01$ level in all three deposits. In the lower watershed, post-settlement overbank and surface deposit sediments displayed significant mercury correlations with organic matter and sulfur while mercury correlations were also present with organic matter in pre-settlement deposits and with sulfur in channel deposits. After these considerations, aluminum, iron, magnesium and organic matter were selected as input variables for backward step-wise regression analysis.

Geochemical Substrate Controls. Observable spatial patterns in mercury concentrations exist in within channel and overbank sediment deposits and between upper and lower watershed location related to the geochemical substrates evaluated. Table 20 shows the final models generated by backward step-wise regression for the substrate elements aluminum, iron, magnesium, and organic matter. All substrates were retained by the stepwise procedure in models for both upper and lower watershed surface samples. However, only eight surface samples are available for analysis and they were collected from different environments; street sediment in the upper watershed and soil in the lower watershed. Therefore the regression results for surface samples are not emphasized in relation to mercury – substrate associations.

In general, the regression models suggest that overbank deposits were more controlled by substrates than active channel deposits. Mercury levels in pre-settlement upper watershed sediments appear to be the most strongly related to substrate elements. The

Table 20. Backward step-wise regression models by deposit type and watershed location.

Sediment Deposit Type	N	Backward Step-wise Regression Model*	R2	S.E.	Sig.
Channel Sediment					
Upper Watershed	56	Hg = 2.2 + 20.4 OM	0.11	167.7	0.011
Lower Watershed	80	Hg = 280	0.00	281.5	0.000
Post-settlement Overbank Sediment					
Upper Watershed	27	Hg = -290.5 + 310.5 Fe	0.39	170.5	0.001
Lower Watershed	36	Hg = -1103.5 + -915.4 Al + 1505.9 Fe	0.51	318.0	0.000
Pre-settlement Overbank Sediment					
Upper Watershed	26	Hg = -3.6 + 7.2 OM + 4.8 Fe + -196.4 Mg	0.71	6.5	0.000
Lower Watershed	31	Hg = -13.7 + 6.4 OM	0.13	9.1	0.051

* Hg (ppb) is the dependant variable; Al (%), Fe (%), Mg (%), and OM (%) are the independent variables.

model incorporating organic matter, magnesium, and iron reduced the variability in mercury concentrations by 71 percent in these uncontaminated sediment. Post-settlement deposit mercury levels were also predictable in the upper watershed by iron ($R^2 = 0.51$), and in the lower watershed by iron and aluminum ($R^2 = 0.39$). Organic matter was retained by the step-wise procedure in channel sediments of the upper watershed, yet only reduced mercury concentration variability by 11 percent. No substrate variables were retained for the active channel sediments of the lower watershed.

In summary, important information has been gained by evaluating the controlling effect of geochemical substrates on mercury concentration. First, this analysis suggests that organic matter and iron content in the sediment are more influential than the other substrate elements. The regression models indicate that both contaminated and uncontaminated overbank sediments were influenced by iron, while the retention of aluminum in one model may suggest grain-size related sorting in overbank deposits. Organic matter was of influence in pre-settlement deposits, yet appeared to be of less consequence in channel sediment. Second, mercury concentration in pre-settlement overbank deposits appear to be strongly influenced by geochemical substrates as indicated by the suitability of organic matter, iron and magnesium as predictor variables. Third, mercury concentrations in channel deposits are not well modeled using geochemical substrates as predictor variables. This is especially true in the lower watershed where not even one element was retained by the backward stepwise procedure. The magnitude of multiple anthropogenic mercury inputs to the stream system may overwhelm or mask the effect of geochemical association and accumulation processes. These findings suggest that investigations into the spatial distribution of mercury in the sediments of polluted streams should not rely solely on chemical accumulation factors or geochemical normalization techniques to explain spatial patterns. These results support the findings of other authors that suggest physical geomorphic controls should be considered when investigating fluvial trace metal pollution distribution (Graf, 1985, 1996; Knox, 1997; Lecce and Pavlowsky, 1997, 2001).

SPATIAL DISTRIBUTION OF MERCURY

Active Channel Trends

Mean mercury concentrations in channel sediment samples collected from bed, edge, and bankfull deposits at each sample site along the main channel are plotted against stream distance from the James River confluence (Figure 29). These samples were collected at approximately 1 km intervals except for a 2.5 km gap where Jordan Creek flows underground (~26 – 28 km) and close interval sampling above and below the SW WWTP. To simplify the longitudinal mercury profile in Figure 29, the samples collected at 100 m intervals near the SW WWTP were averaged upstream and downstream of the outfall and plotted at sites 10 and 25. Mercury values for the 100 m interval samples are plotted in Figure 30. Average mercury in tributary, watershed surface, and post-settlement overbank samples were plotted Figures 29 and 30 to aid trend interpretation. The active transport of elevated concentrations of mercury in channel sediment is evident throughout the watershed and can be divided into four distinct trends.

Upper watershed Mercury Increase. Working downstream in Figure 29, an increasing trend is observed in the upper watershed between samples 42 and 33. Mercury increases over this 10 km stretch from below 50 ppb to above 700 ppb. Jordan Creek drains the historical industrial area between these sites through predominantly stabilized channels. Bed, bank, and low terrace sediment within this portion of the stream have served as a storage reservoir for historical mercury releases from past manufacturing and commercial activities since the 1850's. The mean concentrations of this stored

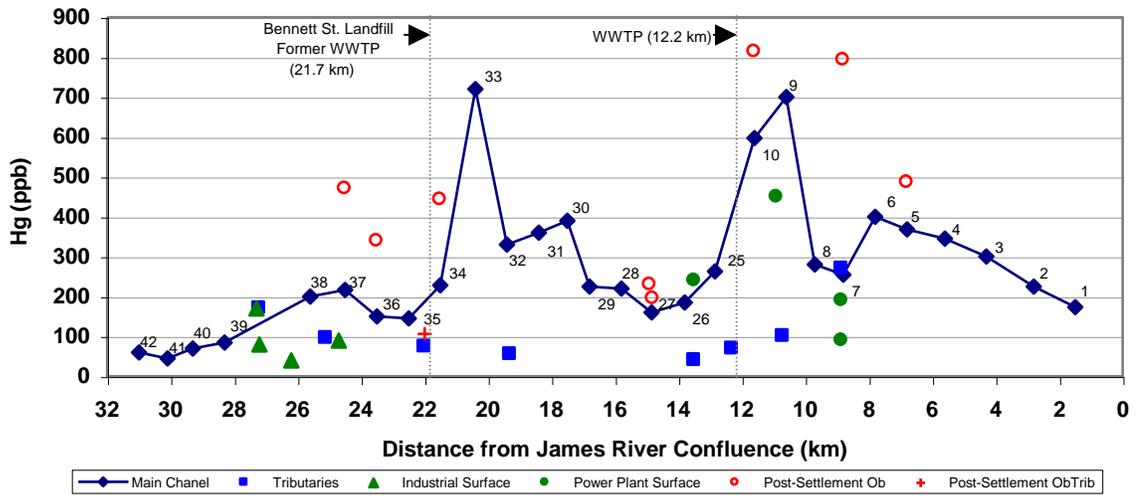


Figure 29. Longitudinal profile of mercury in channel sediment.

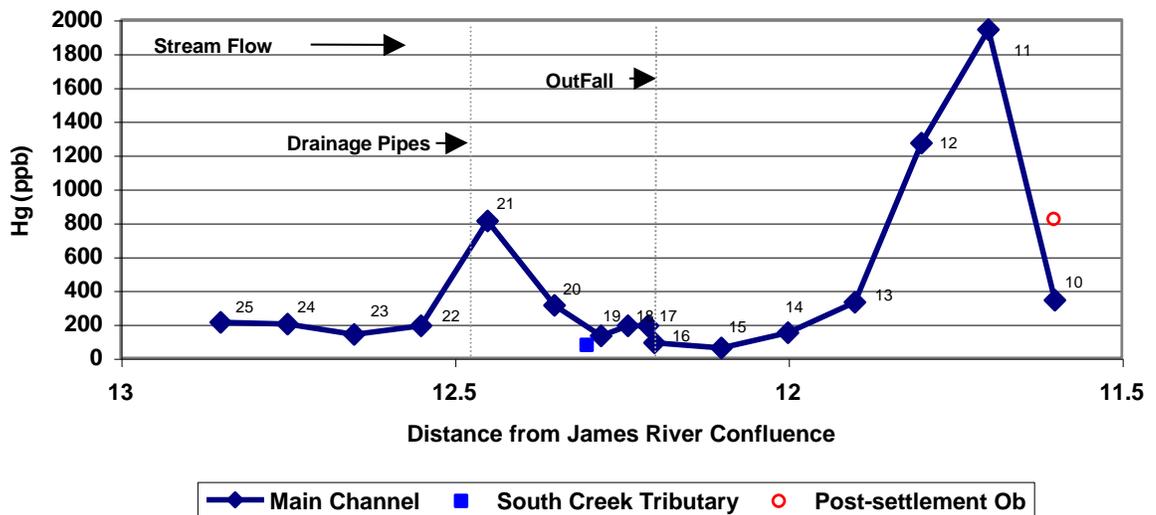


Figure 30. Longitudinal profile of mercury in channel sediment near the SW WWTP.

post-settlement overbank sediment can be seen as red circles in Figure 29 at sites 37, 36, and 34. This sediment is remobilized during storm events from unarmored reaches and at locations where aging stabilization structures have failed (Figure 31). The relatively low mercury concentrations in tributary samples, and all but one street sediment samples (seen as blue boxes and green triangles, respectively, in Figure 29) suggests that surface runoff of atmospheric mercury deposition on surrounding land areas is not significantly contributing to this increasing trend. In fact, dilution from the south branch of Jordan Creek and the tributary near site 38 may be responsible for the slight decrease in mercury concentrations upstream of the rapid climb in mercury levels in the lower portion of this trend.

The sharp increase in mercury concentrations between sites 35 and 33 are likely due to more recent sources. The former Springfield WWTP operated on the north bank of Wilson Creek between sites 35 and 34 until the SW WWTP was fully operational in 1961 (Sutton, 1981). This site also served as the Bennett Street landfill between 1955 and 1961 when the entire facility, sewage trenches, sludge ponds, and solid wastes were buried. Leachate from the buried wastes and stored sediment within channel and overbank environments near this site are likely mercury sources at this site. Contaminated sediment from historical sources are responsible for the gradual, then sharp, increasing present-day mercury trend in the upper watershed.



Figure 31. Failed bank armoring along Jordan Creek upstream of site 39.
Photo by D.J. Wurglitsh. Used with permission.

Upper watershed Mercury Decay. Mercury concentrations decrease from over 700 ppb at site 33 to below 200 ppb at site 27 (Figure 29). Mercury concentrations decrease sharply within this 6 km stretch. A slight increase in mercury at sites 31 and 30 produce a bump in this otherwise concave profile. The low mercury concentrations in the tributary discharging just downstream from site 32 imply that the small increase is not from this tributary. The decreasing trend in mercury concentrations in this stretch may be due to a lack of nearby sources. The historical land use within this area was predominantly agricultural and more recently residential. While overbank sediments were not collected in the middle of this area, the relatively low mercury concentrations in the overbank sediment at site 27 may be indicative of the overbank sediment further

upstream. Without present-day mercury releases within this stretch, dilution, mixing, and chemical aging of geochemical substrates serves to reduce mercury concentrations in sediment to minimum levels maintained by the erosion of historical contaminated overbank sediment and surface runoff of atmospherically deposited mercury.

This mercury decay trend may not be solely due to the absence of mercury sources. A location between sites 28 and 27 was selected as the boundary between the upper and lower watershed due to differing geomorphic and hydrologic conditions, as described earlier. The relatively steep slope near site 27 (Figure 14) and the geomorphically adjusted smaller channel cross-sectional area in these stream reaches may promote sediment transport over deposition. Flood waters are contained near this reach so that velocity is maximized and mercury contaminated sediment is flushed downstream rather than deposited in the channel or on the floodplain. Therefore geomorphic processes may be partially responsible for mercury decay within this area.

Lower Watershed Mercury Increase. Mercury levels steadily climb from below 200 ppb to 700 ppb in the 4.5 km of stream channel between sites 27 and 9 (Figure 29). Increased mercury concentrations within this stretch of stream is likely due to the deposition of historically contaminated sediment remobilized from the upper watershed and from recent mercury discharges from two municipal sources in the area. The relatively low levels of mercury at site 27 and 26 suggest that mobilized historical sediment sources from the upper watershed are not responsible for the steep increase in actively transported sediment within this reach. The availability of locally stored contaminated overbank sediment, as evidenced at site 10, may be contributing to climbing mercury levels within this reach.

Mercury concentrations are relatively low in the three small tributaries samples along this stretch. However, soil samples collected to the northeast and southeast of the power plant (Figure 8) had high mercury concentrations, 240 ppb and 450 ppb respectively. Surface runoff from these sites would drain toward this portion of Wilson Creek. This suggests that close proximity atmospheric mercury deposition from the SW PS has contaminated nearby soils thereby contributing to increased mercury in channel sediment.

Karst features in the vicinity of the SW WWTP and the SW PS may affect mercury concentrations in stream sediments. Several sinkholes are located near these facilities, as seen in Figure 5, that may serve to collect and introduce mercury and other pollutants to the stream via springs, estavelles, and ground water within this reach. Vineyard and Feder (1974) reported that a 1968 dye trace links sinkholes at the SW WWTP to Radar Spring approximately 2.4 km downstream. At one time nearly half of the discharge from the spring was from treated waste water (Black, 1997). The magnitude of surface to stream connections via karst conduits is unknown at this time.

Industrial waste water conducted through the SW WWTP or infiltration of waste water through karst features on the plant property may contribute to elevated mercury levels in this part of the stream. Mercury concentrations rise dramatically below the outfall and below two drainage pipes on the SW WWTP property as revealed by close interval sampling reported in Figure 30. Concentrations near 2,000 ppb were measured within 500 meters of the outfall. Treated water discharged to the stream is tested for mercury at the SW WWTP laboratory every three months and found to be consistently below allowable limits of 12 µg/L (Burke, 2004). Site 21, upstream of the outfall had a concentration of over 800 ppb. Two concrete drainage pipes, approximately 0.75 m and

1.2 m diameter, terminated in the channel just upstream of this site, and may have served as overflows or primary outfalls at some time in the past. SW WWTP personnel had no knowledge of these pipes. Sewage sludge, of unknown mercury content, is applied to agricultural lands as a soil conditioner within a 48 km radius of the SW WWTP. This may be a nonpoint source of mercury introduced to this reach through surface runoff.

The evidence evaluated here suggests that the increasing mercury trend in the lower watershed is caused by several possible sources. Nonpoint sources may include runoff from atmospherically contaminated soils near the SW PS and agricultural soils in the area, upstream bank and bed erosion of historically contaminated sediment, and land surfaces at the SW WWTP and SW PS that are connected to the stream by karst conduits. Potential point sources include the SW WWTP outfall and documented releases of mercury from the SW PS.

Lower Watershed Mercury Decay. Finally, mercury concentrations decline from 700 ppb at site 9 to below 200 ppb 1.5 km above the James River confluence at site one (Figure 29). This decrease in mercury levels is not continuous along the 9 km of this sampled reach. Concentrations fall precipitously in the first 2 km, increase between site 7 and 6, and then gradually decline again over the last 7.5 km. High concentrations of mercury in a tributary draining land southeast of the power plant are likely responsible for the increase in mercury levels between sites 7 and 6 (Figure 29). Runoff from sampled surfaces to the west of the power plant drain to the Creek in this same area, yet the concentrations of these two samples were substantially lower than the downwind samples to the east.

The decreasing trend in mercury levels in this reach may be due to the absence of sources below the SW WWTP and SW PS. The altered hydrology created by the WWTP discharge just upstream of this reach may serve to reduce mercury concentrations. Flow is intermittent in Wilson Creek for much of the year upstream of the SW WWTP. The discharge from the plant supplies downstream reaches with year-round flow. This may promote the transport of constituent-bearing sediment out of the system. Chemical changes in water characteristics, such as decreases in pH or increases in dissolved ions (e.g. chlorine), can decrease mercury adsorption (Gabriel and Williamson, 2004). The repeated release of mercury to the water column and re-adsorption to substrates can facilitate the transport of mercury downstream.

Distance Decay. Mean mercury concentrations were plotted against stream distance for the two decreasing trends observed within the watershed. The upper watershed decay trend is plotted for sites 33 to 27 (Figure 32) and the lower watershed trend is plotted at sites 9 through 1 (Figure 33). To evaluate the nature of the distance decay trends of mercury within these two reaches, linear, power, logarithmic, and exponential functions were fitted to the data. Exponential functions produced models that reduced variability by the greatest amount in both reaches. Logarithmic, linear, and power function models had R^2 values of 0.588, 0.630, and 0.683, respectively for the upper watershed and values of 0.350, 0.488, and 0.517, respectively for the lower watershed trend. The exponential equations, however, had R^2 values of 0.727 for the upper watershed and 0.598 for the lower watershed as seen in Figures 32 and 33. Other investigators have long recognized this inverse exponential relationship in the downstream decay of metal concentrations below source locations (Wertz, 1949; Rose, 1970; Hawkes, 1976; Phillips, 1988).

In Summary, non-point source erosion of contaminated sediment from historical sources are responsible for the gradual to sharp mercury increases in the upper watershed. Historical to recent releases of mercury from municipal utility point and non-point sources have increased mercury in the channel and overbank environments of the lower watershed. Mercury decay trends in the upper and lower watershed are well modeled by inverse exponential equations. Geomorphic and hydrologic factors work in concert with physical and chemical dilution processes to move mercury-bearing sediment through the system.

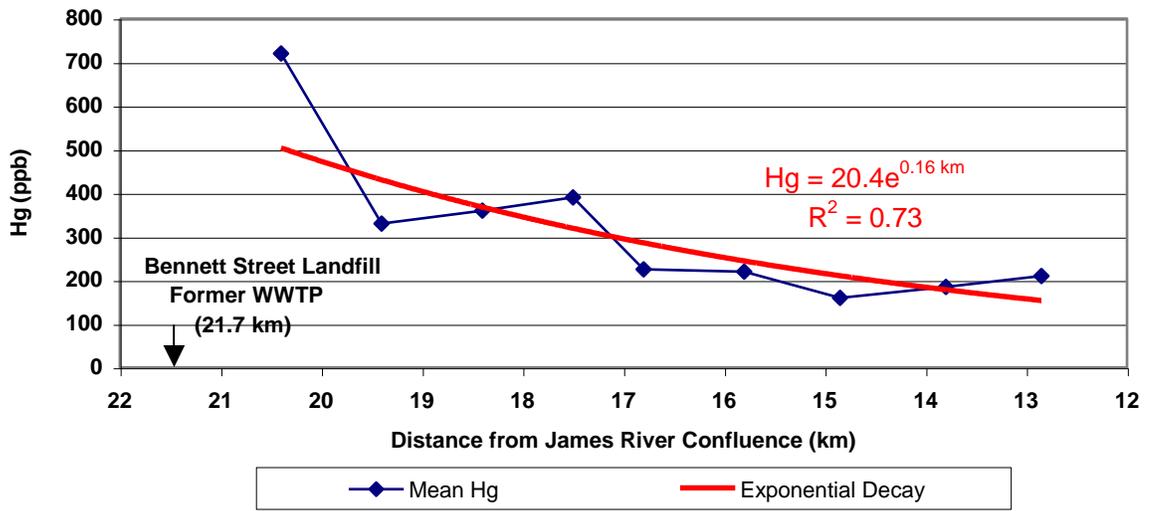


Figure 32. Upper watershed mercury distance decay trend.

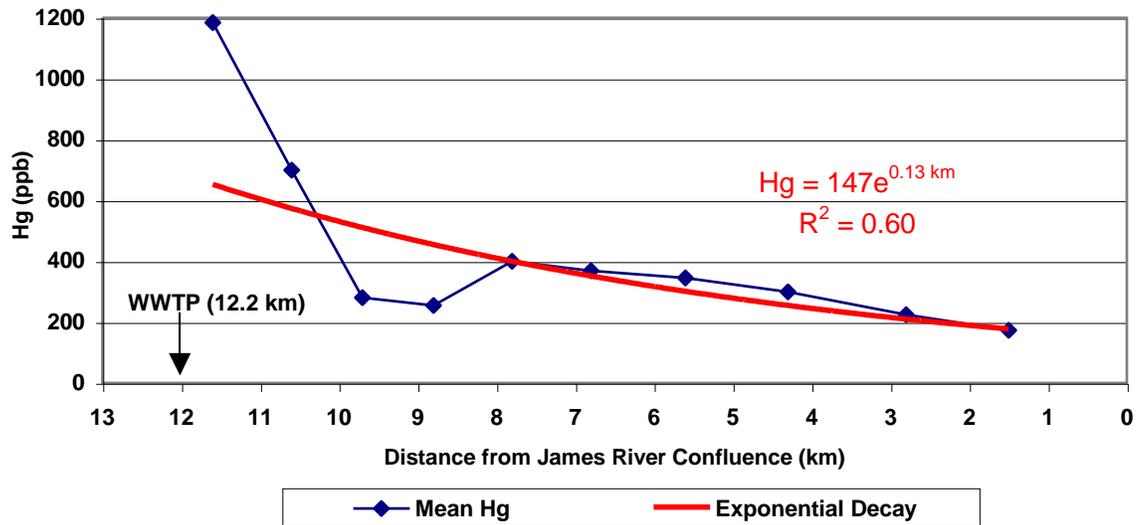


Figure 33. Lower watershed mercury distance decay trend.

Overbank Trends

Overbank Longitudinal Mercury Profiles. The longitudinal distribution of mercury in the overbank environment was examined by plotting the 20 cm depth averaged mercury concentrations for each main channel overbank site against distance downstream (Figure 34). The same depth averaged mercury levels are displayed differently in Figure 35 to show the magnitude of mercury storage in overbank deposits at each site. Differences in contamination levels and in the timing of pollution release and sedimentation are revealed by shifting stratigraphically from the early historical period (100 – 120 cm depth) to the 1950's to 2004 (0 – 20 cm depth). Additional overbank mercury data from a floodplain core sample at stream distance 3.2 km was added to extend the longitudinal profile toward the confluence with the James River. This data is from the 55 m core collected by Shade (2003) and is labeled “site K” on the distribution plots.

Striking contrast can be seen in the magnitude of mercury increase at down stream sites over those in the upper watershed. In general, lower watershed levels in the top 60 cm are two to four times those of upstream concentrations at the same depths. Pollution timing and sources can be understood by viewing each depth plot as an assessment of mercury transport and storage on the active floodplain surface at some time in the past.

Beginning at the bottom of the graph in Figure 34 and to the left of each site in Figure 34 it is apparent that the 100 to 120 cm depth, shown in light blue, represents pre-settlement conditions as mercury is at background levels throughout the watershed. The 80 to 100 cm plot, however, records upper watershed mercury releases at site 34 with a small amount being deposited downstream at sites 10 and 5. Sites 34 and 10 both have

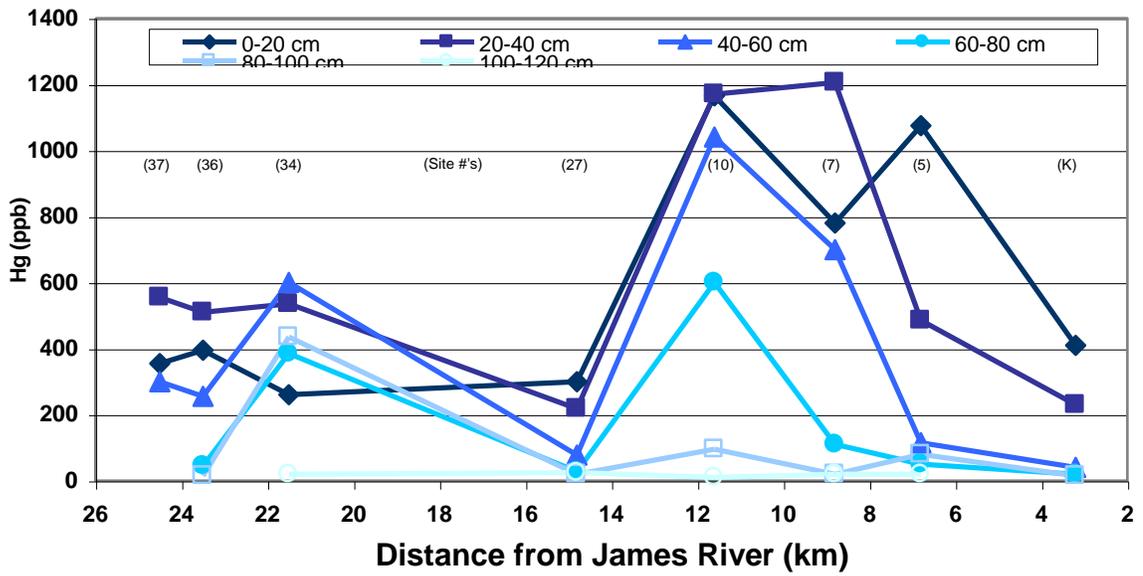


Figure 34. Longitudinal distribution of mean mercury in the overbank profile.

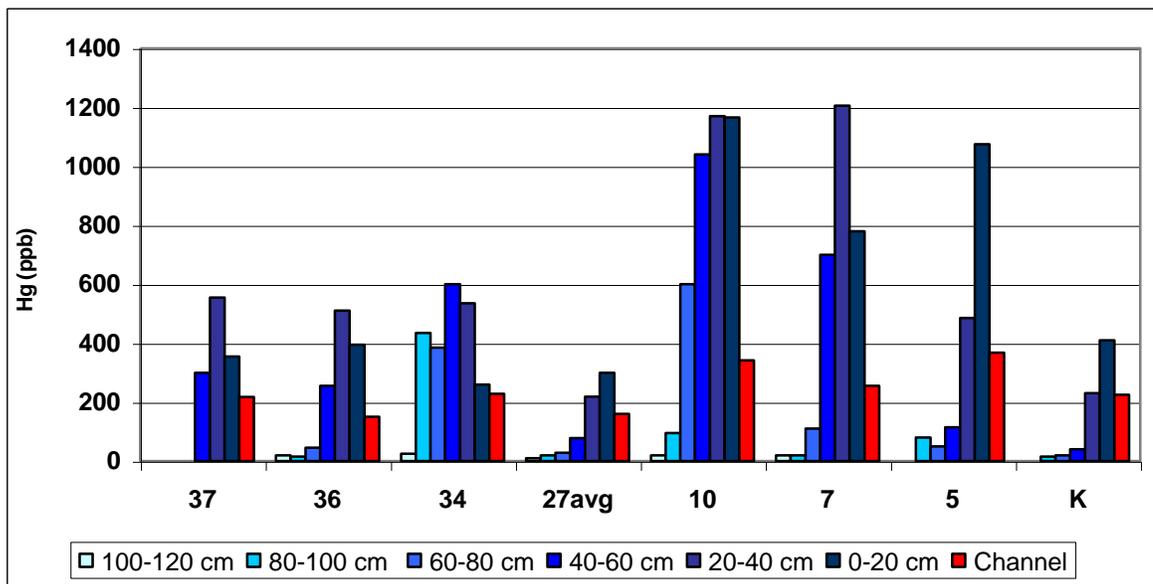


Figure 35. Mean mercury in the Overbank profile and in channel sediment.

buried soils at 90 to 100 cm depth while that depth at site 5 is within buried lateral accretion deposits, or active channel sediments. The 60 to 80 cm plot shows continued deposition at site 34, slight increases at site 27, and substantial mercury sedimentation at site 10 and a small amount at site 7. While no buried soil was observed at site 7, the increases in mercury at that site between 60 and 80 cm suggest that pre-settlement surfaces are within this depth range. At the 40 to 60 cm depth, mercury is elevated at every site in the watershed. Relatively low amounts at site 5 reflect the buried point bar surface and the transition to historical overbank sedimentation. This 40 to 60 cm depth represents the peak pollution levels at site 34 and may represent the beginning of downstream mercury sources, with mean concentrations exceeding 1,000 ppb at site 10 below the SW WWTP.

Peak overbank mercury concentrations within the upper watershed are reached at sites 36 and 37 during the time represented by the 20 to 40 cm depth plot. Channel enlargement and storm sewer network installation within the upper watershed reaches are likely beginning to reduce overbank sedimentation. At the same time, waste water connections are being transferred from the former WWTP near site 34 to the new SW WWTP upstream of site 10. The 10 to 20 cm plot represents the present-day surface and is consistently characterized by lower mercury levels in the upper watershed and higher levels in the lower. Peak mean mercury levels occur at this surface for sites 27 and 5. Site 27 resembles the other lower watershed sites in mercury profiles with the exception of mercury concentration magnitude. Geomorphic controls such as reduced cross-sectional area and increased slope are likely responsible for reduced mercury bearing sedimentation at this site.

Overbank Mercury Models. The magnitude of mercury contamination in overbank sediments is important as a possible source of mercury to the active channel through bank erosion. It is clear from Figures 26, 33, and 34 that stream reaches near overbank sample sites have the potential for mercury inputs from overbank sources. This is especially so in the lower watershed where overbank mercury levels are high. Similar determinations can not be made within certain upper, middle and lower reaches of the stream where overbank sediment was not sampled. Estimating overbank mercury storage within these channel reaches was accomplished using active channel mercury levels as a predictor of overbank levels (Figure 36). Regression equations were generated for maximum overbank mercury, using maximum channel mercury; mean overbank mercury, using mean channel mercury; and mean historical overbank mercury, also using mean channel mercury. The precision of this technique is dependent on the strength of the relationship between mercury levels in channel sediment and those in overbank sediment. The accuracy is dependant upon the similarity in present and historical mercury trends in the watershed. Understanding that recent sources are contributing to active channel trends in the lower watershed, the model is suitable only as a rough approximation of mercury storage at any one particular site.

Estimated maximum, mean, and mean historical overbank mercury levels are plotted in Figure 37. For comparison, the actual mean historical mercury overbank mercury values are also plotted. In general, the overbank mercury estimates are approximately two times channel mercury levels as indicated by regression line slopes near 2 for all three models in Figure 36. Estimated overbank trends match those of the active channel mercury values used as the model input (Figure 29 and 37). The estimated values are

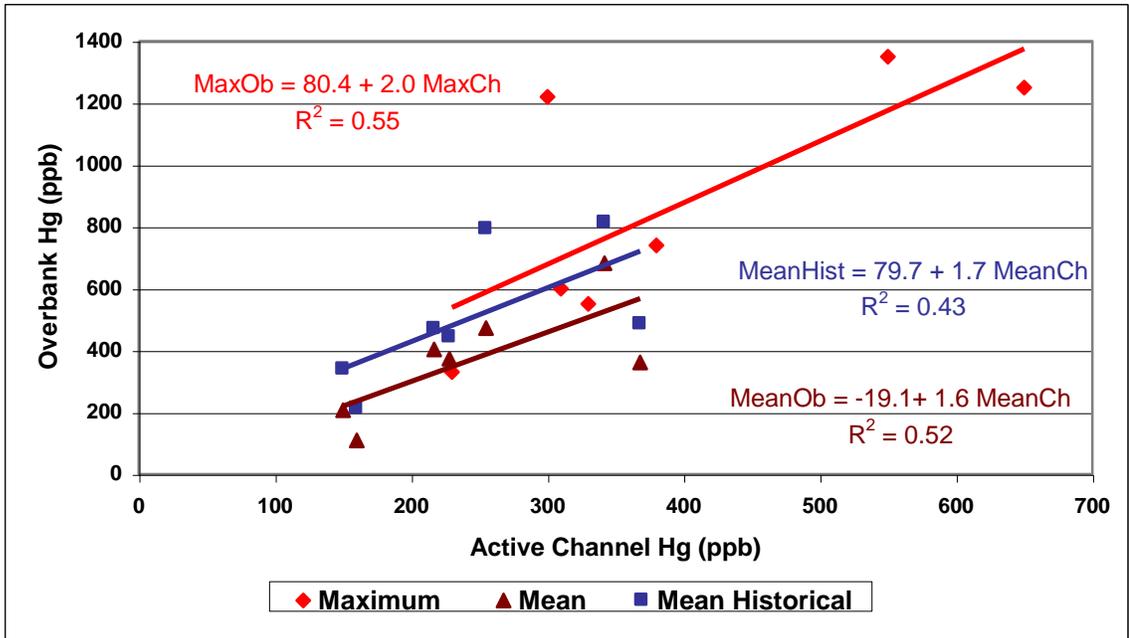


Figure 36. Overbank mercury to Channel Mercury for maximum, average, and average historical concentrations.

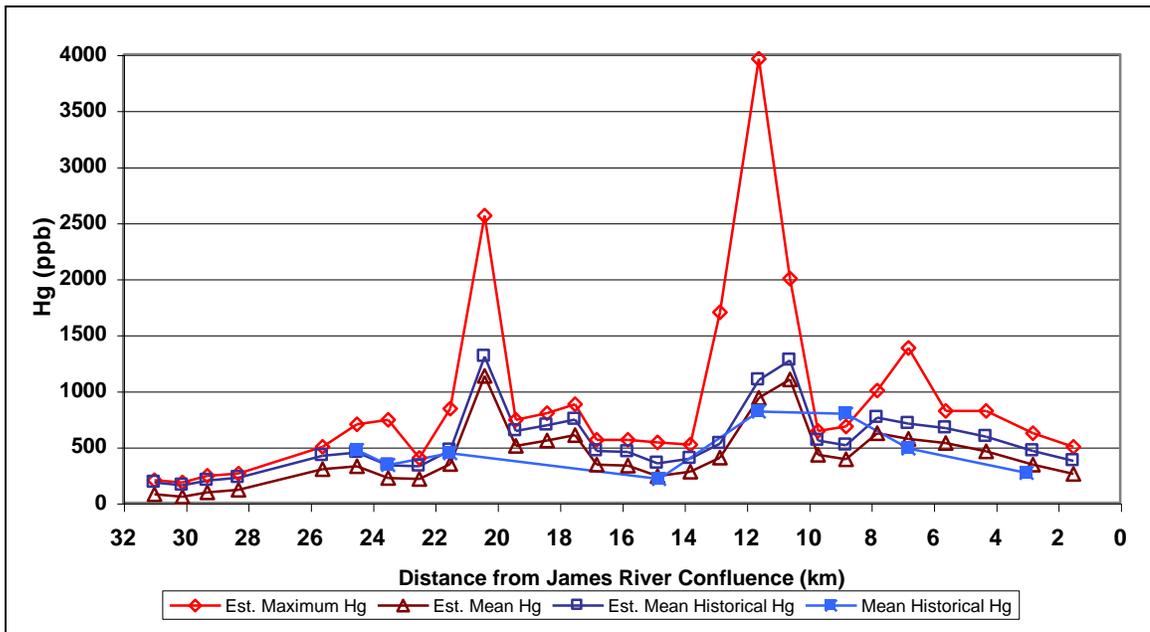


Figure 37. Estimated maximum, mean, and mean historical overbank mercury.

probable most useful and accurate for the gap in overbank sampling between stream distance 15 km and 21 km. Mercury levels and trends in the active channel sediments in this reach are predominantly shaped by historical sources and should be a good predictor of historical overbank mercury levels. Lower watershed mercury estimates are probably less reliable in predicting overbank mercury levels. Recent mercury sources influencing mercury levels in the active channel sediments of the lower watershed would cause the model to over estimate historical mercury levels at lower watershed reaches as seen in the lower 8 km in Figure 37.

Pollutant Comparisons

Longitudinal Trend Comparisons. The longitudinal distributions of copper lead and zinc within active channel sediments were compared to the distribution of mercury in Figure 38 while phosphorous and mercury are compared in Figure 39. This comparison will aid in the interpretation and understanding of mercury distribution within the channel sediments of the watershed. Channel samples of copper (Cu), phosphorous (P), lead (Pb), and zinc (Zn) were averaged at each site and for close interval samples near the WWTP as described for mercury above. Mercury is plotted in Figs 38 and 39 for trend comparison only and is not scaled with the other elements which are reported in concentrations of parts per million (ppm). Pearson correlation results for these elements in the channel sediment samples are reported in Table 21.

The distribution of phosphorous bears close resemblance to that of mercury (Figure 39). Sharp increases in concentrations near the former and present-day WWTP's may indicate a common source. Mercury also correlates strongly with phosphorous and also copper as see in Table 21. The trends of phosphorous and mercury diverge, however, in

Table 21. Pearson correlation matrix for Hg, Cu, Pb, P, and Zn in channel sediments.

(n = 136)	Hg	Cu	P	Pb	Zn
Hg	1				
Cu	*0.391	1			
P	*0.380	*0.616	1		
Pb	0.178	*0.445	-0.089	1	
Zn	0.070	*0.598	0.058	*0.593	1

* Significant at the p = 0.01 level.

Bold is significant at the p = 0.05 level.

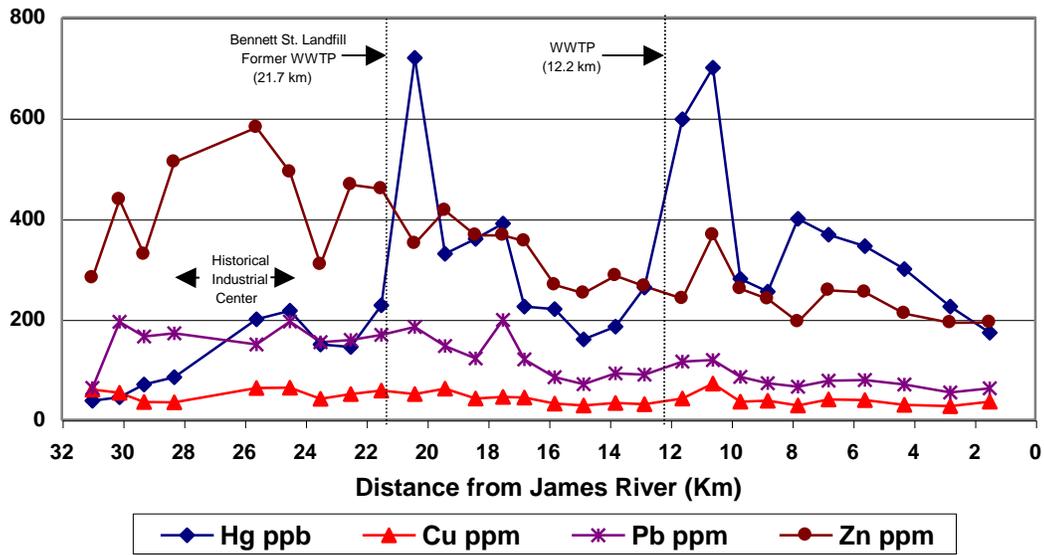


Figure 38. Longitudinal distribution of the mean Hg , Cu, Pb, & Zn in channel sediment.

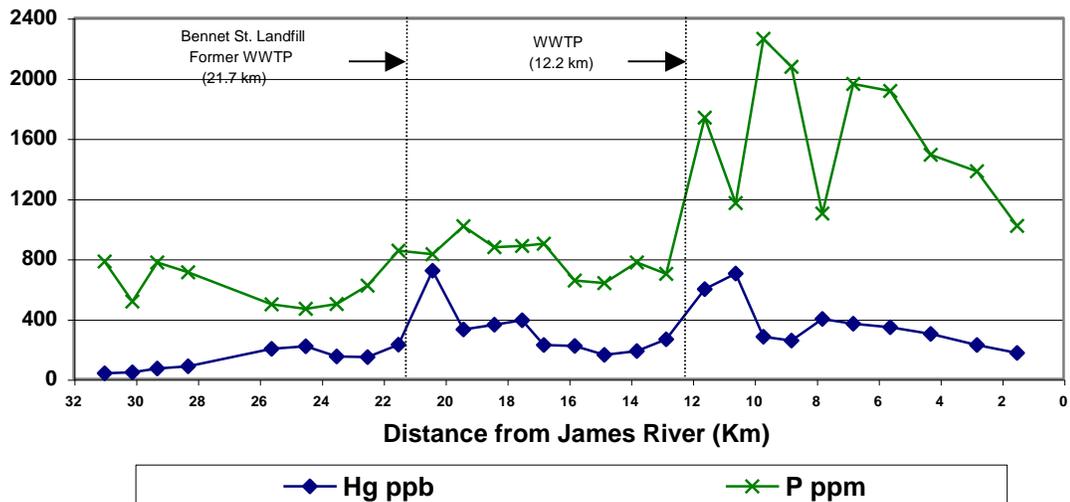


Figure 39. Longitudinal distribution of mean mercury and phosphorous.

the extreme upper watershed where recent urban and industrial phosphorous sources exist. Phosphorous concentrations are high while those of mercury are at the lowest point in the distribution. Zinc, lead, and copper are all strongly correlated and have only slight increases near the SW WWTP, and their trends show little similarities with mercury within the rest of the watershed (Figure 38). Zinc and copper have very similar trends which are high within the historical industrial area and steadily decrease toward the confluence. Phosphorous, zinc, and lead have similar decreasing trends between 17 km and 15 km and all trends tend to decrease steadily in the extreme lower watershed. This suggests that similar processes are at work among differing elements in removing contaminated sediment from storage. Increased sediment transport is likely due to restricted channel geometry and increased slope between 17 km and 15 km while the year-round discharge from the SW WWTP may be responsible for the decrease in the lower watershed.

Overbank Profile Comparisons. The overbank profiles of copper, phosphorous, lead, and zinc were compared to that of mercury to better understand the timing and nature of mercury sources and to evaluate the depths of anthropogenic contamination in relation to that of buried soil. Profiles from sites 36 in the upper watershed and site 10 in the lower watershed are shown in Figure 40. Pearson correlation matrices are shown in Table 22 for all post-settlement and pre-settlement overbank sediment samples.

The depth of peak pollutant concentration are noticeably different between the upper and lower watershed. Peak concentrations of copper, phosphorous, lead, and zinc occur between 10 and 20 cm at site 37 in the upper watershed. Lower watershed peaks were at

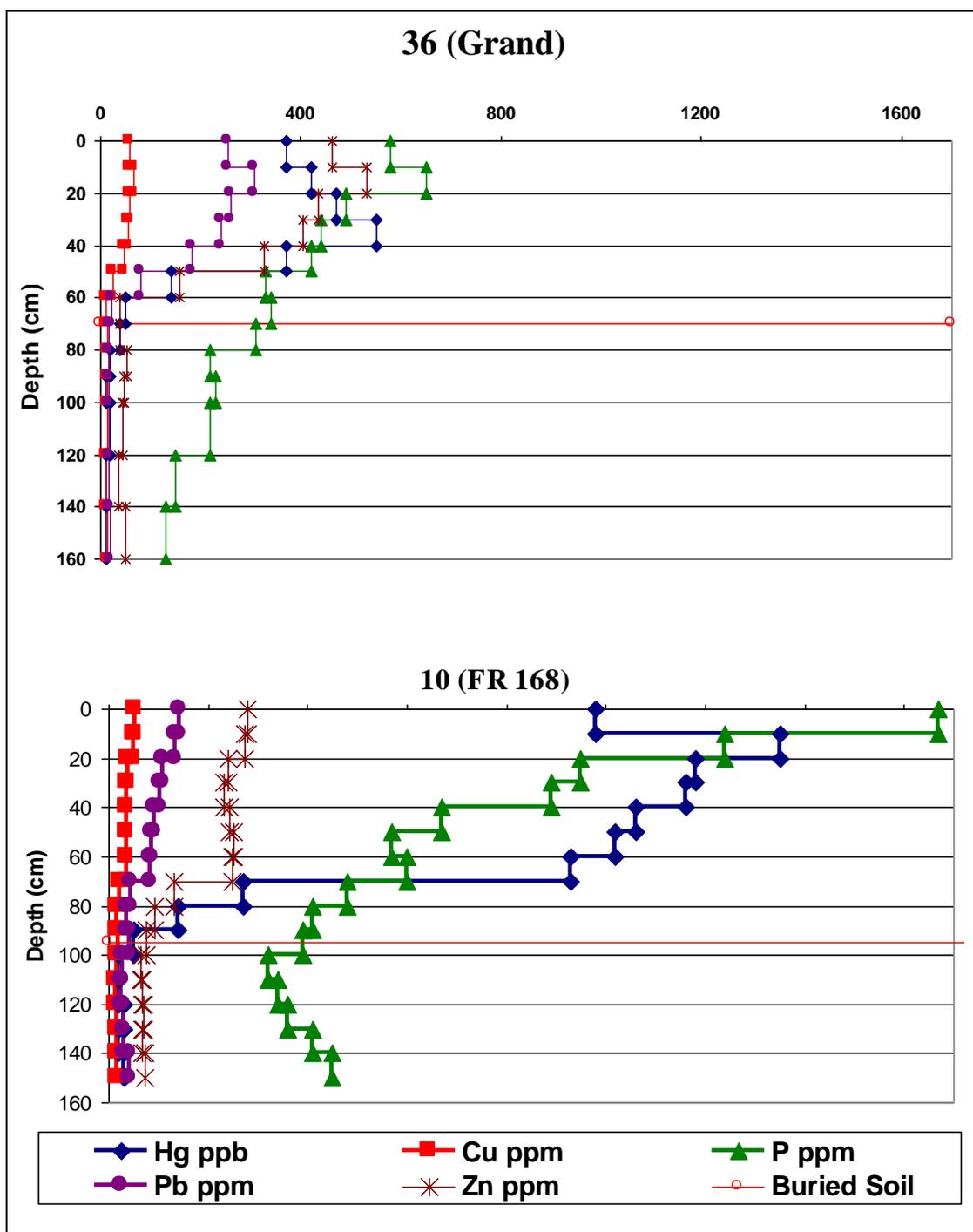


Figure 40. Overbank profiles of Hg, Cu, P, Pb, and Zn at sites 36 and 10.

Table 22. Pearson correlation of historical and background overbank sediments.

	Hg	Cu	P	Pb	Zn
Post-settlement Overbank (n = 63)					
Hg	1.000				
Cu	*0.375	1.000			
P	*0.702	*0.371	1.000		
Pb	0.212	*0.965	0.221	1.000	
Zn	*0.322	*0.963	0.291	*0.945	1.000
Pre-settlement Overbank (n = 57)					
Hg	1.000				
Cu	*0.330	1.000			
P	0.276	0.103	1.000		
Pb	*0.552	*0.507	*0.319	1.000	
Zn	*0.355	*0.677	0.156	*0.712	1.000

* Significant at the p = 0.01 level.

Bold is significant at the p = 0.05 level.

the surface for the same pollutants. This matches the trend for mercury indicating more recent sedimentation in the lower basin.

The depth of the buried soils compare well with the decrease of most pollutants to their respective background levels. Similar to mercury, copper, lead, and zinc all approach background concentrations near 60 cm depth at site 36. This is only 10 cm above the observed buried soil depth at this site. Lead and zinc match mercury at the lower watershed sites as all three are reduced to background levels near the buried soil depth of 90 to 100 cm. However, substantial reductions are seen at 70 cm for copper, lead, zinc, and mercury. These same elements are closely correlated in the pre-settlement deposits (Table 22). Phosphorous experienced steady decline with increasing depth

throughout the upper watershed profile, but reached a low near the buried soil in the lower watershed profile and then increased in concentration with depth.

In summary, comparing mercury distribution to that of other pollutants clarified source and timing trends. The departure of mercury trends from the steady decline seen in lead and zinc levels in channel (Figure 38) and overbank (Figure 40) sediments throughout the watershed indicates lower watershed sources of mercury and not just downstream accumulation from upper watershed sources. The strong correlation between copper, lead and zinc is present in channel sediments as well as post-settlement deposits suggests common sources and transport processes for these elements. Deeper peak pollutant levels in the overbank profiles of the upper watershed suggest historical sedimentation of contaminants in the upper watershed while peaks at the surface in the lower watershed suggest recent deposition. The increase in mercury and phosphorous levels in channel and overbank sediment of the lower watershed as well as a strong correlation (0.702) between these elements suggest a common source for these elements. Increases in phosphorous levels in water have been documented in the lower watershed and attributed to the SW WWTP (Black, 1997). Comparing mercury trends to those of phosphorous and other trace elements seem to further confirm the hypothesis that the presence and transport of mercury in the present-day fluvial environments is from past manufacturing activities in the upper watershed and more recent municipal utility releases in the lower watershed.

CHAPTER SIX:

SUMMARY AND CONCLUSIONS

Mercury is considered one of the most toxic and pervasive pollutants affecting aquatic environments in the U.S. Missouri is now under a state-wide fish consumption advisory for all streams and lakes. Mercury has been detected in water, fish tissue, and sediment samples from the lower reaches of Wilson Creek in recent years. The purpose of this study was to assess the level of mercury contamination in channel and floodplain sediments within the Wilson Creek watershed. This was accomplished by (1) determining the spatial distribution of mercury in the active channel sediments of Wilson Creek to evaluate the present-day transport of mercury through the system, and (2) determining the spatial and temporal distribution of mercury in overbank floodplain deposits to obtain pre-settlement background mercury levels, to better understand historical pollution sources, and to locate areas of mercury storage within the watershed.

Channel samples were collected at approximately one kilometer intervals along the entire channel length. Overbank samples were collected at 10 cm depth averaged intervals to a depth of nearly two meters at nine channel cutbank locations within the watershed. Each sample was analyzed for organic content and for pollutant and geochemical substrate elements. The low terrace floodplain surfaces at five overbank sites were dated by measuring the ¹³⁷cesium activity in sediment samples. The resulting data was differentiated by deposit type; being channel, post-settlement overbank, or pre-settlement overbank sediment; and by upper or lower watershed location, determined by geomorphic process regime. The following conclusions have been drawn regarding the spatial and temporal distribution of mercury within the sediments of Wilson Creek.

Mercury Concentrations and Potential Toxicity

Mercury concentrations. Mercury concentrations in stream sediment within the Wilson Creek watershed ranged from 10 to 1,940 ppb. Natural background mercury levels for the watershed were determined to be 20 ppb based upon the average mercury concentration of the uncontaminated sediment in pre-settlement overbank deposits. However, this level may increase to 50 ppb in sediment rich in organic matter or iron. Samples collected within the active channel had mean mercury levels over 200 ppb while mean mercury concentrations in the post-settlement deposits were near 450 ppb. Mercury levels in channel sediments increased with height above the channel bed. Bankfull surfaces and channel edge samples consistently had higher mercury levels than channel bed sediments suggesting that hydraulic sorting may have some effect in redistributing mercury bound to finer-grained deposits in sedimentation zones. Using channel capacity to divide the watershed into upper and lower sub-watersheds at 14.8 km from the James River confluence, mean mercury levels in both channel and post-settlement overbank deposits were more than 30 % higher in the lower watershed. A small number of surface sediment samples had mean mercury levels of 95 ppb in sediment collected from upper watershed roadways and of 243 ppb in samples collected from soils near the power plant in the lower watershed.

Table 23. Percentage of samples exceeding TET and PEL sediment mercury levels.

Sediment Deposit Type	Upper Watershed		Lower watershed	
	> 1000 ppb	> 486 ppb	> 1000 ppb	> 486 ppb
Active Channel Samples (n = 136)	1%	1%	2%	7%
Post-Settlement Overbank (n = 63)	0%	13%	13%	25%

TET - toxic effect threshold (McDonald et al., 2000)

PEL - probable effect level (McDonald et al., 2000)

Potential Mercury Toxicity. It is not within the scope of this study to assess the toxicological risk associated with various mercury levels at particular sites. It may be appropriate, however, to mention the sediment mercury levels at which other investigations have deemed potentially hazardous to human and animal health through bioaccumulation in aquatic environments. The U.S. Food and Drug Administration (USFDA, 1993) has established a Guidance / Action / Tolerance mercury level in sediment at 1,000 ppb (1 ppm). McDonald et al. (2000) reported a toxic effect threshold (TET) for mercury in sediment at the same 1,000 ppb concentration. The probable effect level (PEL) above which harmful effects are likely to be observed in macroinvertebrate populations of amphipods and midges was established at 696 ppb for mercury in sediment in 1994 (FDEP, 1994) and more recently it was lowered to 486 ppb (McDonald et al., 2000). Individual channel and overbank sediment samples exceed the 1,000 ppb TET and the 486 ppb PEL at several sites in the lower watershed (Table 23).

Mercury Sediment Geochemistry

The data evaluated in this study suggest that geochemical substrates, as indicated by related elemental analysis, were important in controlling mercury distribution in pre-settlement deposits, yet had a more limited effect upon historical mercury distribution especially in channel sediments. Common associations were found: (1) between organic matter and sulfur, (2) between iron and manganese, and (3) among aluminum, magnesium, and calcium. Of these substrate elements, organic matter, iron, magnesium and aluminum were most strongly correlated to mercury. Organic matter and iron were most effective in explaining mercury variability in pre-settlement overbank deposits (Table 20). The magnitude of multiple anthropogenic mercury inputs to the stream system may overwhelm or mask the effect of geochemical association and accumulation processes. These findings suggest that investigations into the spatial distribution of mercury in the sediments of polluted streams should not rely solely on chemical accumulation factors or geochemical normalization techniques to explain spatial patterns, but should also consider physical geomorphic controls (Graf, 1985, 1996; Knox, 1997; Lecce and Pavlowsky, 1997, 2001).

Historical Overbank Deposits

Sedimentation Rates. Sedimentation rates were estimated using ^{137}Cs activity and pollution history to date upper and lower surfaces within the post-settlement. The results of ^{137}Cs analysis at five overbank sites indicate that little sedimentation has occurred on the low terrace surface since peak cesium fallout in 1964. Observed buried soils depths ranged between 70 to 100 cm depth at overbank sites and were assigned a date of 1870. The rates of historical sedimentation between the buried soil and low terrace surfaces

differed at upper and lower watershed locations. In general, Upper watershed rates were 0.5 cm per year while lower watershed rates were closer to 1 cm per year since 1870 (Table 15).

Overbank Mercury Trends. Striking contrasts were observed in the magnitude of mercury increase at down stream sites over those in the upper watershed. Lower watershed mercury levels in the top 60 cm are typically two to four times higher than those of upstream concentrations at the same depths. In general, peak mercury levels occurred deeper in the overbank profile at upper watershed sites and near the surface at the lower watershed sites (Figure 35). This may suggest mercury deposition in close proximity to the historical industrial center during Springfield's early industrialization years. Higher mercury levels near the floodplain surfaces of the lower watershed reflect more recent contamination sources. This was supported by the total channel capacity and two year flood estimates which show that upper stream reaches tended to be sediment transport zones while lower reaches may experience deposition and scour during the two year flow events (Figure 17).

Active Channel Sediment Trends

Two distinct mercury peaks are present within the actively transported channel sediment of the watershed (Figure 29). The upper 12 km of the channel experience increasing mercury levels within the historical industrial center of downtown Springfield. This increase culminates in peak mean mercury levels over 700 ppb just downstream of the former WWTP and the closed Bennett St. landfill at 21.7 km from the James River confluence. This peak is followed by 6 km of mercury concentration decay through residential areas of the lower upper watershed.

A second peak in mean mercury levels is observed just down stream of the current WWTP located at 12.2 km from the James River confluence. This trend is characterized by rapid increases in mercury concentrations within an approximately 5 km reach of the stream and is followed by a relatively gradual decay for 11 km toward the confluence with the James River. Mean mercury concentrations at the apex of this trend are also near 700 ppb.

Watershed Sources of Mercury

Sources of mercury in the upper watershed are predominantly from nonpoint historical pollution sources. The sources include contaminated bed and overbank sediment eroded from within the historical industrial center of Springfield and from leaching of buried waste from the former water treatment plant and landfill to the stream environment. The relatively low intensity of contemporary mercury sources, mixing of contaminated sediment with cleaner sediment from tributaries, and channel sediment transport regime may be responsible for the decreasing mercury trend between the upper and lower watershed channel reaches.

Mercury sources within the lower watershed include both point and nonpoint releases. The Southwest Waster Water Treatment Plant outfall and a tributary draining the Southwest Power Station appear to be point sources of mercury to the stream since the late 1950's. Nonpoint source releases include surface runoff of atmospherically contaminated soils in close proximity to the SW PS and possibly runoff from nearby agricultural lands treated with waste sludge from the treatment plant. Landfills and WWTP's in this watershed, and others, have been identified as sources of trace elements

to stream sediments (Sutton, 1981; Mantei and Foster, 1991; Pierce, 1992; Mantei and Sappington, 1994).

The existence of recent downstream municipal sources is also supported by the longitudinal distribution of other pollutants (Figure 38 and 39). Historical upstream sources of lead, zinc, phosphorous, and mercury are seen in elevated levels of these pollutants at upper watershed sites. Lead and zinc levels generally decline toward the James River confluence while elevated phosphorous and mercury levels in channel sediment are present below the SW WWTP. The departure of mercury and phosphorous trends from those of lead and zinc in the lower watershed suggests that elevated levels of mercury are from lower watershed sources in addition to historically contaminated sediment from the upper watershed.

Increased mercury levels in channel sediment within the losing stream reach just upstream of the SW WWTP may be due to accumulation of sediment-bound mercury from historical upstream sources. In addition, seasonally variable water table heights and abundant karst features may provide connections from land surfaces near the SW WWTP and SW PS to nearby stream reaches. Karst connections between trace metals from urban land surface sources and metal levels in stream channel sediments have been observed in nearby watersheds (Gutierrez et al., 2004). The downstream decline in mercury levels below these lower watershed sources are due to the absence of sources and to chemical desorption and increased sediment transport processes owing to the release of treated effluent to the stream from the waste water treatment plant outflow. Exponential stream distance models characterize mercury decay below both the former and current WWTP locations.

Implications

Management. The amount and location mercury transported in channel sediment and stored in overbank sediment has important implications for resource managers concerned with the quality of the aquatic environment. The use of bank and bed sediment surveys to compliment water quality assessment and monitoring is essential for an adequate understanding of stream health. Sporadic detection of dissolved mercury in the waters of Wilson Creek will not surprise managers who recognizes sediment as a mercury storage reservoir. Reaches vulnerable to mass wasting or scour of contaminated overbank sediment can be protected to prevent the remobilization of stored mercury.

Restoration of the stream channel to a more natural appearance and the repair of bank stabilization structures are proposed for sections of Jordan Creek. This action may make available large quantities of contaminated sediment for downstream transport if precautions are not taken to prevent sediment loss during the construction phases and erosion of sediment from unarmored banks in restored reaches. Managers and decision makers considering the use of constructed wetlands as a means of reducing phosphorous loading to Wilson Creek and James River can now consider the risks of mercury methylation associated with such actions.

Public Affairs. The information from this investigation, generated within the Ozarks Environmental and Water Resources Institute, is important to the Southwest Missouri State University community, the residents of the Southwest Missouri region, and to people in other urban centers concerned with water quality issues. This research reveals that pending federal legislation and EPA rule making to reduce mercury emissions from utility power generators may not yield immediate reductions in mercury contamination in

aquatic environments. Mercury stored in alluvial bank and bed sediment throughout the Wilson Creek watershed may contribute to mercury contamination in the downstream receiving waters of James River and Table Rock Lake for years to come.

Future Research

As the preliminary study for an ongoing mercury assessment, the information obtained through this reconnaissance survey will support and guide future investigations. Close interval overbank geochemical sediment surveys, precise channel topography mapping, volume estimates of floodplain deposits, and measures of bank stability are needed throughout the watershed to better understand historical mercury sources, dominant geomorphic processes, and mercury loading and source potential to the present-day channel. Costly areal sampling of watershed surfaces can be limited to lower watershed areas near the SW PS and agricultural lands where waste sludge from the SW WWTP has been applied as a soil conditioner. Areas of elevated mercury in the active channel deposits located through this investigation can guide future biological monitoring and research into the links and pathways of biotic uptake of sediment-bound mercury.

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Appendix I. Within sample duplicate geochemical analysis

Sample Number	Al	Ca %	Fe %	Mg %	Mn %	Cu ppm	Hg ppm	Pb ppb	Zn ppm	
WNC5 B		1.5	2.1	2.2	0.1	1070	20	30	47	108
WNC5 B R		1.9	2.0	2.4	0.2	1370	19	40	49	116
Mean		1.7	2.0	2.3	0.2	1220	20	35	48	112
St.Dv.		0.2	0.0	0.2	0.0	212	1	7	1	6
CV%		14.1	1.0	6.7	13.7	17.4	3.6	20.2	2.9	5.1
WNC2 A		0.9	8.0	2.3	0.2	2550	57	210	142	422
WNC2 A R		1.5	10.5	2.0	0.3	2600	78	250	174	536
Mean		1.2	9.2	2.1	0.2	2575	68	230	158	479
St.Dv.		0.4	1.7	0.2	0.1	35	15	28	23	81
CV%		35.1	19.0	9.7	37.9	1.4	22.0	12.3	14.3	16.8
WNC1 C		1.7	1.8	2.5	0.2	2050	19	120	38	132
WNC1 C R		2.3	1.8	2.6	0.2	2180	21	70	40	140
Mean		2.0	1.8	2.6	0.2	2115	20	95	39	136
St.Dv.		0.4	0.0	0.0	0.0	92	1	35	1	6
CV%		19.5	1.6	1.9	11.5	4.3	7.1	37.2	3.6	4.2
WNC11 A		1.1	2.4	1.5	0.1	671	24	550	66	136
WNC11 A R		1.4	2.3	1.6	0.1	724	30	500	73	154
Mean		1.3	2.3	1.5	0.1	698	27	525	70	145
St.Dv.		0.2	0.1	0.1	0.0	37	4	35	5	13
CV%		15.5	3.4	4.1	18.4	5.4	15.7	6.7	7.1	8.8
<u>Overall</u>										
Mean		1.5	3.8	2.1	0.2	1652	34	221	79	218
St.Dv.		0.3	0.5	0.1	0.0	94	5	27	8	26
CV%		21.0	6.2	5.6	20.4	7.1	12.1	19.1	7.0	8.7

Appendix II. Variation in spatial homogeneity among channel sediment samples.

Sample Number	OM %	Al %	Ca %	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	Pb ppm	Zn ppm
66A	6.2	0.8	9.31	39	3.2	130	0.14	3260	146	356
66B	6.7	0.78	10.55	38	3.04	120	0.15	2800	148	421
66C	7.1	1.02	10.3	44	2.95	190	0.17	2830	168	453
Mean	6.7	0.9	10.1	40.3	3.1	146.7	0.2	2963	154.0	410.0
St.Dv.	0.5	0.1	0.7	03.2	0.1	37.9	0.0	257	12.2	49.4
CV %	6.8	15.4	6.5	8.0	4.1	25.8	10.0	8.7	7.9	12.1
66D	18.1	1.34	9.66	74	2.21	300	0.27	2340	196	517
66E	11.9	1.42	9.91	66	2.68	380	0.24	2660	198	512
66F	12.4	1.44	9.81	66	2.81	260	0.23	2890	202	517
Mean	14.1	1.4	9.8	68.7	2.6	313.3	0.2	2630	198.7	515.3
St.Dv.	3.5	0.1	0.1	04.6	0.3	61.1	0.0	276	3.1	2.9
CV %	24.5	3.8	1.3	6.7	12.3	19.5	8.4	10.5	1.5	0.6
67A	13.7	1.36	6.29	53	1.87	170	0.21	662	141	356
67B	6.6	1.8	2.38	25	2.47	70	0.16	1165	71	147
67C	7.3	1.4	5.07	43	2.76	180	0.17	1495	148	347
Mean	9.2	1.5	4.6	40.3	2.4	140.0	0.2	1107	120.0	283.3
St.Dv.	3.9	0.2	2.0	14.2	0.5	60.8	0.0	419	42.6	118.2
CV %	42.3	16.0	43.7	35.2	19.2	43.4	14.7	37.9	35.5	41.7
67D	6.8	0.93	12	55	2.86	330	0.24	1490	298	479
67E	6.4	1.86	0.76	15	2.09	30	0.14	1340	29	79
67F	9.0	1.1	10.3	67	2.5	230	0.23	1500	324	510
Mean	7.4	1.3	7.7	45.7	2.5	196.7	0.2	1443	217.0	356.0
St.Dv.	1.4	0.5	6.1	27.2	0.4	152.8	0.1	90	163.3	240.4
CV %	19.0	38.2	78.8	59.6	15.5	77.7	27.1	6.2	75.3	67.5
68A	8.3	1.65	5	31	2.19	180	0.17	1590	84	288
68B	9.1	1.57	5.15	32	2.32	230	0.16	1975	88	307
68C	8.8	1.64	5.78	28	2.42	150	0.16	2180	75	275
Mean	8.7	1.6	5.3	30.3	2.3	186.7	0.2	1915	82.3	290.0
St.Dv.	0.4	0.0	0.4	2.1	0.1	40.4	0.0	300	6.7	16.1
CV %	4.1	2.7	7.8	6.9	5.0	21.7	3.5	15.6	8.1	5.5

Appendix II. (Continued)

Sample Number	OM %	Al %	Ca %	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	Pb ppm	Zn ppm
68D	8.3	1.76	4.34	31	2.13	190	0.17	1875	84	272
68E	10.4	1.55	4.8	31	2.26	190	0.16	1875	81	294
68F	12.7	1.62	5.91	36	1.95	200	0.17	1635	83	329
Mean	10.5	1.6	5.0	32.7	2.1	193.3	0.2	1795	82.7	298.3
St.Dv.	2.2	0.1	0.8	2.9	0.2	5.8	0.0	139	1.5	28.7
CV %	21.4	6.5	16.1	8.8	7.4	3.0	3.5	7.7	1.8	9.6
69A	12.3	1.72	3.86	45	1.75	290	0.18	1675	79	287
69B	12.7	1.64	3.12	44	1.67	290	0.16	1600	72	274
69C	11.0	1.68	3.87	46	1.86	310	0.18	1545	83	303
Mean	12.0	1.7	3.6	45.0	1.8	296.7	0.2	1607	78.0	288.0
St.Dv.	0.8	0.0	0.4	1.0	0.1	11.5	0.0	65	5.6	14.5
CV %	7.1	2.4	11.9	2.2	5.4	3.9	6.7	4.1	7.1	5.0
69D	14.9	1.78	3.42	46	1.69	300	0.18	1785	77	311
69E	11.7	1.72	3.6	45	1.79	330	0.18	1560	88	303
69F	13.9	1.65	3.38	42	1.65	270	0.17	1610	76	289
Mean	13.5	1.7	3.5	44.3	1.7	300.0	0.2	1652	80.3	301.0
St.Dv.	1.7	0.1	0.1	2.1	0.1	30.0	0.0	118	6.7	11.1
CV %	12.2	3.8	3.4	4.7	4.2	10.0	3.3	7.2	8.3	3.7
Overall										
Mean	10.3	12.3	22.5	43.4	9.7	28.7	10.1	13.4	19.8	20.1
St. Dev	1.8	0.1	1.3	7.2	0.2	50.0	0.0	208.0	30.2	60.2
CV %	17.2	11.1	21.2	16.5	9.1	25.6	9.6	12.2	18.2	18.2

Appendix III. Variation of concentration of selected pollutant elements and Al ratio values in low flow and bankfull deposits at sites 5, 27, 34, and 36.

WNC Sample #	Al %	Cu ppm	Cu/Al	Hg ppb	Hg/Al	Pb ppm	Pb/Al	Zn ppm	Zn/Al
66A	0.8	39	49	130	163	146	183	356	445
66B	0.78	38	49	120	154	148	190	421	540
66C	1.02	44	43	190	186	168	165	453	444
Mean	0.9	40.3	46.9	146.7	167.5	154	179	410	476.3
StDv	0.1	3.2	3.2	37.9	16.8	12.2	12.9	49.4	55
CV %	15.4	8	6.9	25.8	10	7.9	7.2	12.1	11.5
66D	1.34	74	55	300	224	196	146	517	386
66E	1.42	66	46	380	268	198	139	512	361
66F	1.44	66	46	260	181	202	140	517	359
Mean	1.4	68.7	49.2	313.3	224	198.7	142	515.3	368.5
StDv	0.1	4.6	5.2	61.1	43.5	3.1	3.7	2.9	15
CV %	3.8	6.7	10.7	19.5	19.4	1.5	2.6	0.6	4.1
67A	1.36	53	39	170	125	141	104	356	262
67B	1.8	25	14	70	39	71	39	147	82
67C	1.4	43	31	180	129	148	106	347	248
Mean	1.5	40.3	27.9	140	97.5	120	82.9	283.3	197.1
StDv	0.2	14.2	12.8	60.8	50.8	42.6	37.7	118.2	100.2
CV %	16	35.2	45.9	43.4	52.1	35.5	45.4	41.7	50.8
67D	0.93	55	59	330	355	298	320	479	515
67E	1.86	15	8	30	16	29	16	79	42
67F	1.1	67	61	230	209	324	295	510	464
Mean	1.3	45.7	42.7	196.7	193.4	217	210.2	356	340.4
StDv	0.5	27.2	30	152.8	169.9	163.3	169	240.4	259.3
CV %	38.2	59.6	70.3	77.7	87.9	75.3	80.4	67.5	76.2
68A	1.65	31	19	180	109	84	51	288	175
68B	1.57	32	20	230	146	88	56	307	196
68C	1.64	28	17	150	91	75	46	275	168
Mean	1.6	30.3	18.7	186.7	115.7	82.3	50.9	290	179.3
StDv	0	2.1	1.7	40.4	28.1	6.7	5.2	16.1	14.5
CV %	2.7	6.9	8.8	21.7	24.3	8.1	10.1	5.5	8.1
68D	1.76	31	18	190	108	84	48	272	155
68E	1.55	31	20	190	123	81	52	294	190
68F	1.62	36	22	200	123	83	51	329	203
Mean	1.6	32.7	19.9	193.3	118	82.7	50.4	298.3	182.4
StDv	0.1	2.9	2.3	5.8	8.7	1.5	2.4	28.7	25.1
CV %	6.5	8.8	11.6	3	7.4	1.8	4.7	9.6	13.7

Appendix III. (Continued)

WNC Sample #	Al %	Cu ppm	Cu/Al	Hg ppb	Hg/Al	Pb ppm	Pb/Al	Zn ppm	Zn/Al
69A	1.72	45	26	290	169	79	46	287	167
69B	1.64	44	27	290	177	72	44	274	167
69C	1.68	46	27	310	185	83	49	303	180
Mean	1.7	45	26.8	296.7	176.7	78	46.4	288	171.4
StDv	0	1	0.6	11.5	8	5.6	2.8	14.5	7.7
CV %	2.4	2.2	2.3	3.9	4.5	7.1	6	5	4.5
69D	1.78	46	26	300	169	77	43	311	175
69E	1.72	45	26	330	192	88	51	303	176
69F	1.65	42	25	270	164	76	46	289	175
Mean	1.7	44.3	25.8	300	174.7	80.3	46.8	301	175.3
StDv	0.1	2.1	0.4	30	15.1	6.7	4	11.1	0.7
CV %	3.8	4.7	1.4	10	8.6	8.3	8.6	3.7	0.4
Low Mean	1	39	30	193	139	109	90	318	256
Low St.Dev.	0.1	5.1	4.6	37.7	25.9	16.7	14.6	49.5	44.4
Low CV %	9.1	13.1	16	23.7	22.7	14.7	17.2	16.1	18.7
BF Mean	2	48	34	251	178	145	112	368	267
BF St.Dev.	0.2	9.2	9.5	62.4	59.3	43.6	44.8	70.8	75
BF CV %	13.1	20	23.5	27.5	30.8	21.7	24.1	20.4	23.6
Overall Mean	1	43	32	222	158	127	101	343	261
Overall StDv	0.1	7.2	7	50	42.6	30.2	29.7	60.2	59.7
Overall CV %	11.1	16.5	19.7	25.6	26.8	18.2	20.6	18.2	21.2

Appendix IV. Temporal variation in geochemical substrates and pollutant elements at sites 5 and 10 for a five month period.

Collection Date	Site #	Sample #	OM %	Al %	Ca %	Fe %	Mg %	Mn ppm	Cu ppm	Cu/AlHg ppb	Hg/Al ppm	Pb ppm	Pb/Al ppm	Zn ppm	Zn/Al ppm	
01/23/03	5	11A	5.2	1.1	2.4	1.5	0.1	671	24	21	550	482	66	58	136	119
01/23/03	5	11B	3.9	0.6	3.4	1.8	0.1	908	13	22	290	483	60	100	145	242
01/23/03	5	11C	12	1.3	4	1.6	0.2	1335	37	29	250	198	67	53	249	198
Mean			7.1	1	3.2	1.6	0.1	971	25	24	363	388	64	70	177	186
06/17/03	5	16A	15	1.6	3.1	1.7	0.2	1090	46	28	440	272	80	49	244	151
06/17/03	5	16B	16	1.8	4.1	1.8	0.2	1485	57	31	450	247	90	49	318	175
06/17/03	5	16C	8	1.5	1.8	1.9	0.1	1350	37	25	650	439	96	65	229	155
Mean			13	1.6	3	1.8	0.2	1308	47	28	513	319	89	55	264	160
Mean			10	1.3	3.1	1.7	0.1	1140	36	26	438	354	77	62	220	173
St.Dv.			4.1	0.5	0.2	0.1	0.1	238	16	3	106	49	17	11	62	19
CV %			41	34	5.9	6.3	37	20.9	44	11.4	24	13.7	23	17.9	28	10.7
01/23/03	10	13A	6.5	1	7.2	3.6	0.1	3710	36	38	280	295	310	326	211	222
01/23/03	10	13B	N/A	2.2	5.7	1.8	0.2	2850	136	62	550	252	68	31	430	197
01/23/03	10	13C	7.5	1.3	3.9	2.5	0.1	2510	32	25	520	406	110	86	224	175
Mean			7	1.5	5.6	2.6	0.1	3023	68	42	450	318	163	148	288	198
06/17/03	10	17A	11	1.9	5.2	2	0.2	1235	38	20	210	110	59	31	190	99
06/17/03	10	17B	8.9	1.7	3.1	2	0.2	1560	35	21	220	131	71	42	208	124
06/17/03	10	17C	7.6	1.8	3	2.4	0.2	2020	32	18	270	154	111	63	205	117
Mean			9.2	1.8	3.8	2.2	0.2	1605	35	20	233	132	80	46	201	113
Mean			8.1	1.6	4.7	2.4	0.2	2314	52	31	342	225	122	97	245	156
St.Dv.			1.6	0.2	1.3	0.3	0	1003	23	16	153	132	58	72	62	60
CV %			20	14	28	15	25	43.3	45	50.9	45	58.5	48	74.8	25	38.4
Overall Mean			9.1	1.5	3.9	2.1	0.1	1727	44	28	390	289	99	80	232	164
St.Dv.			2.9	0.3	0.7	0.2	0	621	19	9	130	90	38	42	62	39
CV %			30	24	17	10	31	32.1	45	31.1	35	36.1	35	46.3	27	24.6

Appendix V. Temporal variation in geochemical substrates and pollutant elements at sites 5 and 36 for a sixteen month period.

Collection Date	Site #	Sample #	OM %	Al %	Ca %	Fe %	Mg %	Mn ppm	Cu ppm	Cu/Al	Hg ppb	Hg/Al	Pb ppm	Pb/Al	Zn ppm	Zn/Al
01/09/03	36	5A	6.8	0.75	9.28	2.08	0.18	1655	56	75	160	213	178	237	442	589
01/09/03	36	5B	4.4	1.54	2.05	2.2	0.14	1070	20	13	30	19	47	31	108	70
Mean			5.6	1.1	5.7	2.1	0.2	1363	38	44	95	116	113	134	275	330
05/13/04	36	67A	13.7	1.36	6.29	1.87	0.21	662	53	39	170	125	141	104	356	262
05/13/04	36	67B	6.6	1.8	2.38	2.47	0.16	1165	25	14	70	39	71	39	147	82
05/13/04	36	67C	7.3	1.4	5.07	2.76	0.17	1495	43	31	180	129	148	106	347	248
05/13/04	36	67D	6.8	0.93	12	2.86	0.24	1490	55	59	330	355	298	320	479	515
05/13/04	36	67E	6.4	1.86	0.76	2.09	0.14	1340	15	8	30	16	29	16	79	42
05/13/04	36	67F	9	1.1	10.3	2.5	0.23	1500	67	61	230	209	324	295	510	464
Mean			8.3	1.4	6.1	2.4	0.2	1275	43	35	168	145	169	147	320	269
Mean			7	1.3	5.9	2.3	0.2	1319	41	40	132	131	141	140	297	299
St.Dv.			1.9	0.2	0.3	0.2	0	62	4	6	52	21	40	9	32	43
CV %			27.1	14.6	5.6	8.8	12.7	4.7	8.7	15.3	39.4	15.7	28.2	6.4	10.6	14.4
01/23/03	5	11A	5.2	1.14	2.36	1.49	0.1	671	24	21	550	482	66	58	136	119
01/23/03	5	11B	3.9	0.6	3.35	1.83	0.06	908	13	22	290	483	60	100	145	242
01/23/03	5	11C	12.2	1.26	3.98	1.58	0.16	1335	37	29	250	198	67	53	249	198
Mean			7.1	1	3.2	1.6	0.1	971	25	24	363	388	64	70	177	186
05/13/04	5	69A	12.3	1.72	3.86	1.75	0.18	1675	45	26	290	169	79	46	287	167
05/13/04	5	69B	12.7	1.64	3.12	1.67	0.16	1600	44	27	290	177	72	44	274	167
05/13/04	5	69C	11	1.68	3.87	1.86	0.18	1545	46	27	310	185	83	49	303	180
05/13/04	5	69D	14.9	1.78	3.42	1.69	0.18	1785	46	26	300	169	77	43	311	175
05/13/04	5	69E	11.7	1.72	3.6	1.79	0.18	1560	45	26	330	192	88	51	303	176
05/13/04	5	69F	13.9	1.65	3.38	1.65	0.17	1610	42	25	270	164	76	46	289	175
Mean			12.8	1.7	3.5	1.7	0.2	1629	45	26	298	176	79	47	295	173
Mean			9.9	1.3	3.4	1.7	0.1	1300	35	25	331	282	72	58	236	180
St.Dv.			4	0.5	0.2	0.1	0	465	14	2	46	150	10	17	83	9
CV%			40.1	36.6	6.5	4.3	34.3	35.8	40.8	6.4	13.9	53.3	14.6	28.7	35.4	5
Overall Mean			8.5	1.3	4.6	2	0.2	1310	38	32	231	206	106	99	266	240
St.Dv.			2.9	0.3	0.3	0.1	0	263	9	4	49	85	25	13	57	26
CV %			33.6	25.6	6.1	6.5	23.5	20.2	24.8	10.8	26.6	34.5	21.4	17.5	23	9.7

Appendix VI. Temporal variation in geochemical substrates and pollutant elements at sites 27 and 34 for a nineteen month period.

Collection Date	Site #	WNC Sample #		OM %	Al %	Ca %	Fe %	Mg %	Mn ppm	Cu ppm	Cu/Al	Hg ppb	Hg/Al	Pb ppm	Pb/Al	Zn ppm	Zn/Al
10/01/02	34	2	B	14.8	0.95	10.3	1.79	0.22	2500	72	76	200	211	152	160	488	514
10/01/02	34	2	C	11.6	0.92	8.45	2.48	0.17	2250	68	74	260	283	168	20	446	485
10/01/02	34	2	A	14.3	0.88	7.98	2.25	0.15	2550	57	65	210	239	142	18	422	480
Mean				13.6	0.9	8.9	2.2	0.2	2433.3	65.7	71.5	223.3	243.9	154.0	65.9	452.0	492.7
05/13/04	34	66	A	6.2	0.8	9.31	3.2	0.14	3260	39	49	130	163	146	16	356	445
05/13/04	34	66	B	6.7	0.78	10.6	3.04	0.15	2800	38	49	120	154	148	14	421	540
05/13/04	34	66	C	7.1	1.02	10.3	2.95	0.17	2830	44	43	190	186	168	16	453	444
05/13/04	34	66	D	18.1	1.34	9.66	2.21	0.27	2340	74	55	300	224	196	20	517	386
05/13/04	34	66	E	11.9	1.42	9.91	2.68	0.24	2660	66	46	380	268	198	20	512	361
05/13/04	34	66	F	12.4	1.44	9.81	2.81	0.23	2890	66	46	260	181	202	21	517	359
Mean				10.4	1.1	9.9	2.8	0.2	2796.7	54.5	48.0	230.0	195.8	176.3	17.8	462.7	422.4
Mean				12.0	1.0	9.4	2.5	0.2	2615.0	60.1	59.8	226.7	219.9	165.2	41.9	457.3	457.5
St.Dv.				2.3	0.2	0.7	0.5	0.0	256.9	7.9	16.6	4.7	34.0	15.8	34.0	7.5	49.7
CV%				18.8	14.9	7.6	18.2	7.4	9.8	13.1	27.8	2.1	15.5	9.6	81.2	1.6	10.9
09/24/02	27	1	A	6.4	1.53	1.39	2.2	0.16	1570	20	13	70	46	40	29	138	90
09/24/02	27	1	B	6.9	1.43	3.15	2.07	0.14	1875	28	20	110	77	66	21	232	162
09/24/02	27	1	C	5.3	1.72	1.84	2.52	0.17	2050	19	11	120	70	38	21	132	77
Mean				6.2	1.6	2.1	2.3	0.2	1831.7	22.3	14.6	100.0	64.1	48.0	23.5	167.3	109.7
05/13/04	27	68	A	8.3	1.65	5	2.19	0.17	1590	31	19	180	109	84	17	288	175
05/13/04	27	68	B	9.1	1.57	5.15	2.32	0.16	1975	32	20	230	146	88	17	307	196
05/13/04	27	68	C	8.8	1.64	5.78	2.42	0.16	2180	28	17	150	91	75	13	275	168
05/13/04	27	68	D	8.3	1.76	4.34	2.13	0.17	1875	31	18	190	108	84	19	272	155
05/13/04	27	68	E	10.4	1.55	4.8	2.26	0.16	1875	31	20	190	123	81	17	294	190
05/13/04	27	68	F	12.7	1.62	5.91	1.95	0.17	1635	36	22	200	123	83	14	329	203
Mean				9.6	1.6	5.2	2.2	0.2	1855	32	19	190	117	83	16	294	181
Mean				7.9	1.6	3.6	2.2	0.2	1843	27	17	145	90	65	20	231	145
St.Dv.				2.4	0.1	2.1	0.0	0.0	16	6	3	64	37	24	5	90	50
CV%				30.1	3.2	58.9	1.6	3.7	0.9	24.1	19.9	43.9	41.2	37.4	25.9	38.9	34.6
Overall Mean				9.9	1.3	6.5	2.4	0.2	2229	44	38	186	155	115	31	344	301
St.Dv.				2.3	0.1	1.4	0.2	0.0	137	7	10	34	36	20	20	49	50
CV %				24.5	9.1	33.3	9.9	5.6	5.4	18.6	23.9	23.0	28.3	23.5	53.6	20.3	22.7

Appendix VII. Geochemical results of each sample for the elements considered within this study.

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream (Km)	Cs ** Bq/Kg	OM %	Al %	Ca %	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
01/23/03	1 Manley Fd.	CE	10A	1.5	8.7	0.99	6.8	37	1.3	200	0.13	435	1000	58	0.2	189	
01/23/03	1 Manley Fd.	CBF	10B	1.5	8.0	1.02	3.3	55	1.54	210	0.12	583	1180	83	0.1	250	
01/23/03	1 Manley Fd.	CE	10C	1.5	4.2	0.71	2.2	16	1.73	110	0.08	859	870	47	0	142	
02/28/04	2 WCNB 1	CE	56A	2.8	9.5	1.26	3.5	28	1.74	270	0.16	988	1500	53	0.1	180	
02/28/04	2 WCNB 1	CBF	56B	2.8	9.7	1.42	2.1	26	1.98	180	0.13	1445	1260	56	0.1	206	
02/28/04	3 WCNB 3	CE	58A	4.3	8.7	1.38	3.3	26	1.72	230	0.28	1315	1700	59	0.1	194	
02/28/04	3 WCNB 3	CBF	58B	4.3	9.5	1.3	3	33	1.67	370	0.15	1320	1280	81	0.1	229	
02/28/04	4 WCNB 2	CE	57A	5.6	12.8	1.52	3	41	1.78	320	0.16	1225	2190	82	0.1	254	
02/28/04	4 WCNB 2	CBF	57B	5.6	12.1	1.54	2.8	37	1.72	370	0.16	1545	1640	76	0.1	253	
01/23/03	5 FR 182	CE	11A	6.8	5.2	1.14	2.4	24	1.49	550	0.1	671	1100	66	0.1	136	
01/23/03	5 FR 182	CE	11B	6.8	3.9	0.6	3.4	13	1.83	290	0.06	908	1160	60	0	145	
01/23/03	5 FR 182	CBF	11C	6.8	12.2	1.26	4	37	1.58	250	0.16	1335	1620	67	0.1	249	
06/17/03	5 FR 182	OB	16 0-10	6.8	2.23	5.6	1.46	1.1	41	2.06	1250	0.12	1255	890	105	0	214
06/17/03	5 FR 182	OB	16 10-20	6.8	0.00	5.2	1.5	0.8	33	2.12	900	0.12	1405	750	93	0	205
06/17/03	5 FR 182	OB	16 20-30	6.8	0.00	5.2	1.41	0.5	30	1.98	750	0.11	1420	590	79	0	200
06/17/03	5 FR 182	OB	16 30-40	6.8	0.00	4.7	1.38	0.4	20	1.74	220	0.11	1365	360	44	0	124
06/17/03	5 FR 182	OB	16 40-50	6.8	0.00	5.7	1.39	0.4	15	1.78	140	0.11	1335	330	48	0	85
06/17/03	5 FR 182	OB	16 50-60	6.8	0.00	4.7	1.44	0.5	13	1.77	90	0.12	1215	320	48	0	61
06/17/03	5 FR 182	OB	16 60-70	6.8	5.3	1.56	0.6	13	1.79	50	0.12	1075	370	29	0	59	
06/17/03	5 FR 182	OB	16 90-100	6.8	4.8	1.56	0.6	14	1.75	80	0.13	692	530	28	0	78	
06/17/03	5 FR 182	CE	16A	6.8	15.3	1.62	3.1	46	1.73	440	0.19	1090	2940	80	0.1	244	
06/17/03	5 FR 182	CBF	16B	6.8	15.5	1.82	4.1	57	1.76	450	0.22	1485	3100	90	0.1	318	
06/17/03	5 FR 182	CBF	16C	6.8	8.0	1.48	1.8	37	1.87	650	0.14	1350	1280	96	0	229	
05/13/04	5 FR 182	CER	69A	6.8	12.3	1.72	3.9	45	1.75	290	0.18	1675	2240	79	0.1	287	
05/13/04	5 FR 182	CER	69B	6.8	12.7	1.64	3.1	44	1.67	290	0.16	1600	2140	72	0.1	274	

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca %	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
05/13/04	5 FR 182	CER	69 C	6.8	11.0	1.68	3.9	46	1.86	310	0.18	1545	1900	83	0.1	303
05/13/04	5 FR 182	CBFR	69 D	6.8	14.9	1.78	3.4	46	1.69	300	0.18	1785	2410	77	0.1	311
05/13/04	5 FR 182	CBFR	69 E	6.8	11.7	1.72	3.6	45	1.79	330	0.18	1560	1610	88	0.1	303
05/13/04	5 FR 182	CBFR	69 F	6.8	13.9	1.65	3.4	42	1.65	270	0.17	1610	2020	76	0.1	289
01/23/03	5 FR 182	ssR	11 ARep	6.8	5.2	1.42	2.3	30	1.58	500	0.13	724	1100	73	0.1	154
02/28/04	6 us FR 182	CE	55 A	7.8	8.7	1.49	3.2	29	1.6	340	0.14	1180	1360	62	0.1	186
02/28/04	6 us FR 182	CBF	55 B	7.8	8.0	1.46	1.6	28	1.74	460	0.13	1410	840	70	0	203
06/18/03	7 Hasseltine	OB	23 0-10	8.8	8.3	1.49	1.6	37	2.22	650	0.13	1505	1540	111	0	244
06/18/03	7 Hasseltine	OB	23 10-20	8.8	7.5	1.56	1	40	2.18	910	0.13	1530	1310	115	0	234
06/18/03	7 Hasseltine	OB	23 20-30	8.8	6.4	1.6	0.8	36	2.2	1220	0.13	1725	880	99	0	208
06/18/03	7 Hasseltine	OB	23 30-40	8.8	6.4	1.6	1	36	2.24	1190	0.13	1810	820	93	0	206
06/18/03	7 Hasseltine	OB	23 40-50	8.8	6.3	1.58	0.6	31	2.15	770	0.13	1805	590	79	0	193
06/18/03	7 Hasseltine	OB	23 50-60	8.8	5.9	1.47	0.5	27	1.98	630	0.12	1625	400	66	0	168
06/18/03	7 Hasseltine	OB	23 60-70	8.8	5.3	1.5	0.4	18	1.86	180	0.12	1415	320	36	0	95
06/18/03	7 Hasseltine	OBAb	23 70-80	8.8	5.7	1.68	0.4	15	1.85	40	0.13	1190	260	22	0	59
06/18/03	7 Hasseltine	OBAb	23 80-90	8.8	4.7	1.73	0.4	14	1.83	20	0.13	1065	190	18	0	52
06/18/03	7 Hasseltine	OBAb	23 90-100	8.8	4.6	1.69	0.4	13	1.87	20	0.13	978	180	17	0	54
06/18/03	7 Hasseltine	OBAb	23 100-110	8.8	4.7	1.9	0.4	15	2.02	20	0.14	1090	180	17	0	60
06/18/03	7 Hasseltine	OBAb	23 130-140	8.8	4.9	1.95	0.4	14	2.05	20	0.15	1340	180	19	0	67
06/18/03	7 Hasseltine	OBAb	23 160-170	8.8	4.8	2.12	0.4	13	2.21	20	0.16	1715	150	17	0	69
06/18/03	7 Hasseltine	CE	23 A	8.8	11.0	1.74	3.7	43	1.92	300	0.2	1320	2230	72	0.1	261
06/18/03	7 Hasseltine	CBF	23 B	8.8	8.4	1.47	3.9	33	2.03	210	0.16	1355	1920	74	0.1	220
02/28/04	8 FR 174	CE	54 A	9.7	10.0	1.5	4.2	32	2.37	280	0.21	1925	2600	96	0.1	259
02/28/04	8 FR 174	CBF	54 B	9.7	11.2	1.76	3.9	40	1.94	280	0.21	1645	1920	75	0.1	262
01/23/03	9 Repub. Rd.	CE	12 A	10.6	7.9	1.55	2.9	43	2.11	960	0.15	1715	1380	136	0	285
01/23/03	9 Repub. Rd.	CBF	12 B	10.6	8.6	1.32	2.6	37	1.81	530	0.13	1480	960	141	0	281
01/23/03	9 Repub. Rd.	CB	12 C	10.6	33.3	2.45	3	136	1.44	610	0.23	1925	>10000	79	0.3	537

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca %	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm	
01/23/03	10FR 168	CE	13 A	11.6	6.5	0.95	7.2	36	3.63	280	0.09	3710	1580	310	0	211	
01/23/03	10FR 168	CB	13 B	11.6	N/A	2.18	5.7	136	1.84	550	0.17	2850	>10000	68	0.3	430	
01/23/03	10FR 168	CBF	13 C	11.6	7.5	1.28	3.9	32	2.46	520	0.11	2510	1260	110	0	224	
06/17/03	10FR 168	OB	170-10	11.6	2.23	8.0	1.7	2	54	2.38	980	0.14	1570	1670	141	0	278
06/17/03	10FR 168	OB	1710-20	11.6	0.00	7.5	1.76	1.1	50	2.4	1350	0.14	1580	1240	134	0	274
06/17/03	10FR 168	OB	1720-30	11.6	0.00	6.7	1.64	0.9	38	2.36	1180	0.13	1715	950	110	0	240
06/17/03	10FR 168	OB	1730-40	11.6	0.00	6.4	1.59	0.8	36	2.36	1160	0.13	1745	890	102	0	231
06/17/03	10FR 168	OB	1740-50	11.6	0.00	13.9	1.49	0.5	36	2.13	1060	0.12	1410	670	92	0	244
06/17/03	10FR 168	OB	1750-60	11.6	0.00	5.5	1.41	0.4	36	2.03	1020	0.12	1255	570	87	0	251
06/17/03	10FR 168	OB	1760-70	11.6	5.8	1.5	0.5	35	2.32	930	0.13	1870	600	85	0	249	
06/17/03	10FR 168	OB	1770-80	11.6	5.8	1.7	0.5	22	2.21	270	0.14	1765	480	44	0	130	
06/17/03	10FR 168	OB	1780-90	11.6	5.8	1.83	0.5	18	2.19	140	0.14	1825	410	37	0	93	
06/17/03	10FR 168	OB	1790-100	11.6	5.0	1.9	0.4	19	2.57	50	0.14	2680	390	41	0	75	
06/17/03	10FR 168	OBAb	17100-110	11.6	5.2	2.17	0.4	16	2.38	20	0.17	2090	320	27	0	65	
06/17/03	10FR 168	OBAb	17110-120	11.6	5.6	2.22	0.5	15	2.29	20	0.17	1725	340	25	0	66	
06/17/03	10FR 168	OBAb	17120-130	11.6	5.9	2.26	0.4	17	2.45	30	0.17	2080	360	31	0	71	
06/17/03	10FR 168	OBAb	17130-140	11.6	5.9	2.13	0.4	16	2.47	20	0.16	2280	410	30	0	68	
06/17/03	10FR 168	OBAb	17140-150	11.6	5.7	2.1	0.4	17	2.74	30	0.15	3000	450	43	0	73	
06/17/03	10FR 168	CE	17 A	11.6	11.1	1.91	5.2	38	2.03	210	0.2	1235	1940	59	0.1	190	
06/17/03	10FR 168	CBF	17 B	11.6	8.9	1.68	3.1	35	2.03	220	0.17	1560	1130	71	0.1	208	
06/17/03	10FR 168	CE	17 C	11.6	7.6	1.75	3	32	2.39	270	0.16	2020	1020	111	0	205	
02/21/04	11 WWTP 14	CE	42	11.7	9.8	1.8	4.2	64	2.59	1940	0.16	2070	2440	183	0.1	381	
02/21/04	12 WWTP 13	CE	41	11.8	6.9	1.79	2.6	63	2.59	1270	0.15	1895	3390	191	0.1	342	
02/21/04	13 WWTP 12	CE	40	11.9	11.2	1.9	4.6	47	2.19	330	0.18	1855	1740	108	0.1	313	
02/21/04	14 WWTP 11	CE	39	12	7.6	1.68	2.3	28	2.69	150	0.13	5960	1200	80	0.1	137	
02/21/04	15 WWTP 10	CE	38	12.1	7.5	1.94	1.7	20	2.71	60	0.15	3320	870	56	0	118	
06/17/03	16 WWTP	CB	18 A	12.2	5.2	1.97	0.7	24	3.33	70	0.15	5020	1380	77	0	121	

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca %	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
06/17/03	16 WWTP	CE	18 B	12.2	8.1	1.87	9.3	22	2.47	120	0.16	3000	780	73	0	188
06/17/03	16 WWTP	CE	18 C	12.2	7.9	2.24	2.4	24	3.21	80	0.16	3520	1240	68	0	146
02/21/04	17 WWTP 9	CE	37	12.21	9.1	1.42	9.5	26	1.88	190	0.16	1990	730	83	0.1	214
02/21/04	18 WWTP 8	CB	36	12.24	8.4	1.3	11	25	1.9	190	0.14	2190	620	74	0.1	209
02/21/04	19 WWTP 7	CB	35	12.28	10.7	1.69	9.3	23	2.66	130	0.18	3830	600	68	0.1	166
02/21/04	20 WWTP 1	CB	29	12.35	11.4	1.36	6.6	39	1.88	310	0.17	1910	790	94	0.1	336
02/21/04	21 WWTP 2	CB	30	12.45	9.0	1.38	7.4	38	2.22	810	0.16	1925	820	153	0.1	338
02/21/04	22 WWTP 3	CB	31	12.55	9.2	1.34	5.9	34	1.86	190	0.15	1715	690	88	0.1	307
02/21/04	23 WWTP 4	CB	32	12.65	7.4	1.76	3.3	24	2.14	140	0.15	1710	540	53	0	164
02/21/04	24 WWTP 5	CB	33	12.75	8.4	1.52	4.9	34	2.25	200	0.15	1520	770	91	0.1	315
02/21/04	25 WWTP 6	CB	34	12.85	8.0	1.5	4.7	34	2.28	210	0.15	1870	720	104	0.1	339
02/28/04	26 JRFRWY	CB	53 A	13.8	8.9	1.84	4.2	30	2.83	150	0.15	2340	790	77	0.1	263
02/28/04	26 JRFRWY	CBF	53 B	13.8	8.6	1.88	4.4	37	2.2	220	0.19	1960	760	108	0.1	310
09/24/02	27 us FR156	OB	1--1 10-10	14.9	11.00	8.6	1.12	1.2	28	2.06	0.1	1800	620	78	0	214
09/24/02	27 us FR156	OB	1--1 10--20	14.9	5.45	6.0	1.09	0.5	25	1.68	0.09	1445	520	70	0	174
09/24/02	27 us FR156	OB	1--1 20-30	14.9	0.00	5.4	1.09	0.4	23	1.61	0.09	1405	470	60	0	152
09/24/02	27 us FR156	OB	1--1 30-40	14.9	0.00	4.7	1.12	0.4	21	1.62	0.09	1345	390	50	0	132
09/24/02	27 us FR156	OB	1--1 40-50	14.9	0.00	4.7	1.11	0.4	18	1.52	0.09	1240	380	36	0	96
09/24/02	27 us FR156	OB	1--1 50-60	14.9	0.00	4.4	1.1	0.4	14	1.48	0.09	1240	360	26	0	62
09/24/02	27 us FR156	OB	1--1 60-70	14.9	0.00	4.4	1.08	0.3	12	1.4	0.09	1155	320	18	0	38
09/24/02	27 us FR156	OBAb	1--1 70-80	14.9	4.6	1.2	0.4	12	1.49	40	0.1	1195	330	18	0	42
09/24/02	27 us FR156	OBAb	1--1 80-90	14.9	4.6	1.15	0.4	12	1.41	30	0.09	1065	320	18	0	42
09/24/02	27 us FR156	OBAb	1--1 90-100	14.9	5.0	1.21	0.4	12	1.43	30	0.1	1035	300	18	0	50
09/24/02	27 us FR156	OBAb	1--1 100-110	14.9	4.7	1.19	0.4	12	1.41	10	0.1	1000	290	16	0	46
09/24/02	27 us FR156	OBAb	1--1 110-120	14.9	4.7	1.23	0.4	12	1.45	10	0.1	1045	300	16	0	46
09/24/02	27 us FR156	OBAb	1--1 120-130	14.9	5.0	1.19	0.4	12	1.43	10	0.1	1080	290	14	0	46
09/24/02	27 us FR156	OBAb	1--1 130-140	14.9	4.7	1.21	0.4	12	1.46	10	0.1	1110	280	16	0	44

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca % ppm	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
09/24/02	27 us FR156	OBAb 1--1	140-150	14.9	4.6	1.28	0.4	12	1.54	10	0.1	1165	260	18	0	46
09/24/02	27 us FR156	OBAb 1--1	150-160	14.9	4.3	1.33	0.4	13	1.61	10	0.11	1245	270	18	0	48
09/24/02	27 us FR156	OBAb 1--1	160-170	14.9	4.5	1.36	0.4	13	1.65	10	0.11	1350	260	20	0	48
09/24/02	27 us FR156	OBAb 1--1	170-180	14.9	4.7	1.46	0.4	13	1.79	10	0.11	1505	280	20	0	50
09/24/02	27 ds FR156	OB	1--2 0-10	14.8	8.1	1.16	1.2	22	1.85	210	0.11	1605	590	64	0	170
09/24/02	27 ds FR156	OB	1--2 10--20	14.8	4.7	1.11	0.4	20	1.54	280	0.08	1300	350	50	0	116
09/24/02	27 ds FR156	OB	1--2 20-30	14.8	4.7	1.16	0.4	18	1.56	190	0.09	1325	340	40	0	104
09/24/02	27 ds FR156	OB	1--2 30-40	14.8	4.7	1.19	0.4	16	1.49	100	0.09	1145	330	26	0	74
09/24/02	27 ds FR156	OBAb 1--2	40-50	14.8	5.1	1.32	0.4	12	1.5	30	0.1	1150	310	18	0	48
09/24/02	27 ds FR156	OBAb 1--2	50-60	14.8	5.1	1.34	0.4	12	1.55	10	0.1	1170	300	18	0	48
09/24/02	27 ds FR156	OBAb 1--2	60-70	14.8	5.3	1.36	0.5	13	1.59	10	0.11	1255	320	20	0	50
09/24/02	27 ds FR156	OBAb 1--2	70-80	14.8	5.6	1.47	0.5	14	1.63	10	0.11	1390	340	18	0	50
09/24/02	27 ds FR156	OBAb 1--2	80-90	14.8	5.6	1.49	0.5	14	1.62	10	0.11	1330	330	18	0	46
09/24/02	27 ds FR156	OBAb 1--2	90-100	14.8	5.1	1.47	0.4	14	1.6	10	0.11	1230	300	18	0	46
09/24/02	27 ds FR156	OBAb 1--2	120-130	14.8	4.3	1.59	0.4	14	1.79	10	0.12	1195	250	18	0	52
09/24/02	27 ds FR156	OBAb 1--2	150-160	14.8	4.2	1.58	0.4	13	1.9	10	0.14	1400	230	20	0	56
09/24/02	27 ds FR156	OBAb 1--2	180-190	14.8	3.7	1.62	0.4	13	2.02	10	0.17	950	210	16	<0.01	62
09/24/02	27 FR 156	CB	1 A	14.85	6.4	1.53	1.4	20	2.2	70	0.16	1570	530	40	0	138
09/24/02	27 FR 156	CBF	1 B	14.85	6.9	1.43	3.2	28	2.07	110	0.14	1875	580	66	0	232
09/24/02	27 FR 156	CE	1 C	14.85	5.3	1.72	1.8	19	2.52	120	0.17	2050	540	38	0	132
05/13/04	27 FR 156	CER	68 A	14.85	8.3	1.65	5	31	2.19	180	0.17	1590	630	84	0.1	288
05/13/04	27 FR 156	CER	68 B	14.85	9.1	1.57	5.2	32	2.32	230	0.16	1975	670	88	0.1	307
05/13/04	27 FR 156	CER	68 C	14.85	8.8	1.64	5.8	28	2.42	150	0.16	2180	680	75	0.1	275
05/13/04	27 FR 156	CBFR	68 D	14.85	8.3	1.76	4.3	31	2.13	190	0.17	1875	620	84	0.1	272
05/13/04	27 FR 156	CBFR	68 E	14.85	10.4	1.55	4.8	31	2.26	190	0.16	1875	700	81	0.1	294
05/13/04	27 FR 156	CBFR	68 F	14.85	12.7	1.62	5.9	36	1.95	200	0.17	1635	780	83	0.1	329
09/24/02	27 FR 156	ssR	1 C Rep	14.85	5.3	2.27	1.8	21	2.59	70	0.2	2180	520	40	0	140

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca % ppm	Cu %	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
02/28/04	28 HWY 60	CE	52 A	15.8	8.7	1.76	4.2	31	2.1	240	0.18	1715	630	82	0.1	251
02/28/04	28 HWY 60	CBF	52 B	15.8	9.5	1.66	3.1	33	2.26	200	0.16	2030	680	87	0.1	285
06/18/03	29 W.Sunsh.	CE	20 A	16.8	11.7	1.58	6.8	54	2.34	240	0.22	1990	930	147	0.1	399
06/18/03	29 W.Sunsh.	CBF	20 B	16.8	8.9	1.53	5.2	35	2.66	210	0.17	2080	870	93	0.1	312
06/18/03	30 Bennett	CE	19 A	17.5	8.8	1.64	5	45	2.58	380	0.17	1940	910	184	0.1	360
06/18/03	30 Bennett	CBF	19 B	17.5	7.9	1.59	5.2	46	2.57	400	0.17	2010	860	213	0	374
02/28/04	31 Icicle Ln.	CE	51 A	18.4	8.2	1.3	4.3	37	2.64	360	0.14	1965	790	110	0.1	328
02/28/04	31 Icicle Ln.	CBF	51 B	18.4	13.4	1.62	5.4	48	2.5	360	0.19	2020	960	134	0.1	405
06/18/03	32 W-B-Pass	CE	21 A	19.4	13.0	1.49	9.2	59	2	330	0.28	1470	1010	147	0.2	401
06/18/03	32 W-B-Pass	CBF	21 B	19.4	13.9	1.41	8.4	65	2.04	330	0.26	1800	1020	147	0.1	431
02/28/04	33 Hillcrest	CE	50 A	20.4	6.7	1.19	6.5	42	3.08	200	0.14	2040	820	140	0.1	287
02/28/04	33 Hillcrest	CBF	50 B	20.4	13.6	1.83	2.2	61	2.64	1240	0.17	2510	840	229	0.1	414
10/01/02	34 Scenic Rd.	OB	20-10	21.5	8.1	0.99	7.3	50	2.69	260	0.14	2250	630	250	0.1	420
10/01/02	34 Scenic Rd.	OB	2 10--20	21.5	8.7	1.18	7.3	56	2.83	260	0.13	2560	630	240	0.1	446
10/01/02	34 Scenic Rd.	OB	2 20-30	21.5	8.6	1.33	5.8	55	2.56	350	0.12	1930	580	272	0.1	402
10/01/02	34 Scenic Rd.	OB	2 30-40	21.5	8.2	1.33	3.8	51	2.24	720	0.11	1245	560	272	0	362
10/01/02	34 Scenic Rd.	OB	2 40-50	21.5	8.2	1.69	1.4	39	2.55	460	0.1	1310	490	160	0	282
10/01/02	34 Scenic Rd.	OB	2 50-60	21.5	8.6	1.25	1	53	2.45	740	0.1	1210	550	216	0	472
10/01/02	34 Scenic Rd.	OB	2 60-70	21.5	7.6	1.18	0.7	44	2.18	650	0.1	1095	490	156	0	396
10/01/02	34 Scenic Rd.	OB	2 70-80-	21.5	7.4	1.2	1.8	25	1.63	120	0.11	1050	400	58	0	156
10/01/02	34 Scenic Rd.	OB	2 80-90	21.5	5.0	1.15	0.4	20	1.66	220	0.08	1035	330	56	0	160
10/01/02	34 Scenic Rd.	OB	2 90-100	21.5	7.3	1.13	0.8	41	2.11	650	0.09	1105	460	152	0	372
10/01/02	34 Scenic Rd.	OBAb	2 100-110	21.5	5.2	1.21	0.5	13	1.48	30	0.09	825	270	24	0	54
10/01/02	34 Scenic Rd.	OBAb	2 110-120	21.5	4.6	1.18	0.5	11	1.43	20	0.09	775	220	18	0	40
10/01/02	34 Scenic Rd.	OBAb	2 120-130	21.5	4.5	1.27	0.6	11	1.58	10	0.09	800	200	20	0	42
10/01/02	34 Scenic Rd.	OBAb	2 130-140	21.5	4.4	1.33	0.6	10	1.68	10	0.09	705	160	20	0	44
10/01/02	34 Scenic Rd.	OBAb	2 140-150	21.5	4.4	1.32	0.5	9	1.75	20	0.09	375	210	20	0	48

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca % ppm	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
10/01/02	34 Scenic Rd.	OBAb	2 150-160	21.5	4.0	1.25	0.4	8	1.81	20	0.09	145	260	22	0	48
10/01/02	34 Scenic Rd.	OBAb	2 160-170	21.5	3.6	1.08	0.4	8	2.26	20	0.07	170	390	22	0	52
10/01/02	34 Scenic Rd.	OBAb	2 170-180	21.5	3.4	1.06	0.4	8	1.78	20	0.06	95	310	22	0	44
10/01/02	34 Scenic Rd.	OBAb	2 180-190	21.5	2.7	0.79	0.4	8	1.94	10	0.04	150	380	20	<0.01	40
10/01/02	34 Scenic Rd.	CT	2B	21.5	14.8	0.95	10	72	1.79	200	0.22	2500	910	152	0.2	488
10/01/02	34 Scenic Rd.	CBF	2C	21.5	11.6	0.92	8.5	68	2.48	260	0.17	2250	830	168	0.1	446
10/01/02	34 Scenic Rd.	CE	2A	21.5	14.3	0.88	8	57	2.25	210	0.15	2550	880	142	0.1	422
05/13/04	34 Scenic Rd.	CER	66A	21.5	6.2	0.8	9.3	39	3.2	130	0.14	3260	710	146	0.1	356
05/13/04	34 Scenic Rd.	CER	66B	21.5	6.7	0.78	11	38	3.04	120	0.15	2800	650	148	0.1	421
05/13/04	34 Scenic Rd.	CER	66C	21.5	7.1	1.02	10	44	2.95	190	0.17	2830	730	168	0.1	453
05/13/04	34 Scenic Rd.	CBFR	66D	21.5	18.1	1.34	9.7	74	2.21	300	0.27	2340	1080	196	0.1	517
05/13/04	34 Scenic Rd.	CBFR	66E	21.5	11.9	1.42	9.9	66	2.68	380	0.24	2660	910	198	0.1	512
05/13/04	34 Scenic Rd.	CBFR	66F	21.5	12.4	1.44	9.8	66	2.81	260	0.23	2890	970	202	0.1	517
10/01/02	34 Scenic Rd.	ssR	2 A Rep	21.5	14.3	1.46	10	78	1.96	250	0.26	2600	940	174	0.1	536
02/28/04	35 Beaver	CE	49A	22.5	7.2	1.1	8.6	44	3	130	0.17	1995	610	142	0.1	411
02/28/04	35 Beaver	CBF	49B	22.5	8.0	1.28	9.1	59	3.06	160	0.2	2820	630	175	0.1	524
01/09/03	36 Grand	OB	5 0-10	23.5	12.17	7.6	0.92	4.7	59	2.43	0.12	1455	580	256	0	463
01/09/03	36 Grand	OB	5 10--20	23.5	22.49	8.6	1.04	4.4	66	2.47	0.13	1355	650	306	0	531
01/09/03	36 Grand	OB	5 20-30	23.5	4.10	7.3	1.02	2.1	57	2.51	0.1	1320	490	259	0	435
01/09/03	36 Grand	OB	5 30-40	23.5	0.00	7.0	1.03	1.5	55	2.44	0.1	1300	440	240	0	404
01/09/03	36 Grand	OB	5 40-50	23.5	0.00	6.2	1.06	0.9	47	2.24	0.1	1235	420	182	0	327
01/09/03	36 Grand	OB	5 50-60	23.5	0.00	5.0	1.05	0.5	24	1.76	0.09	1005	330	79	0	158
01/09/03	36 Grand	OB	5 60-70	23.5	0.00	4.8	1	0.4	12	1.33	0.08	779	340	21	0	38
01/09/03	36 Grand	OBAb	5 70-80	23.5	5.6	1.1	0.5	13	1.26	40	0.09	463	310	17	0	40
01/09/03	36 Grand	OBAb	5 80-90	23.5	5.1	1.46	0.5	17	1.4	20	0.11	317	220	17	0	53
01/09/03	36 Grand	OBAb	5 90-100	23.5	5.5	1.5	0.5	15	1.44	10	0.12	413	230	16	0	47
01/09/03	36 Grand	OBAb	5 100-120	23.5	5.2	1.51	0.5	15	1.49	20	0.11	493	220	16	0	44

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca %	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
01/09/03	36 Grand	OBAb	5 120-140	23.5	4.3	1.46	0.4	12	1.52	10	0.12	563	150	16	0	37
01/09/03	36 Grand	OBAb	5 140-160	23.5	4.1	1.84	0.4	14	1.96	10	0.15	672	130	19	0	49
01/09/03	36 Grand	CBF	5 A	23.5	6.8	0.75	9.3	56	2.08	160	0.18	1655	520	178	0	442
01/09/03	36 Grand	CE	5 B	23.5	4.4	1.54	2.1	20	2.2	30	0.14	1070	270	47	0	108
05/13/04	36 Grand	CER	67 A	23.5	13.7	1.36	6.3	53	1.87	170	0.21	662	690	141	0.1	356
05/13/04	36 Grand	CER	67 B	23.5	6.6	1.8	2.4	25	2.47	70	0.16	1165	400	71	0	147
05/13/04	36 Grand	CER	67 C	23.5	7.3	1.4	5.1	43	2.76	180	0.17	1495	500	148	0.1	347
05/13/04	36 Grand	CBFR	67 D	23.5	6.8	0.93	12	55	2.86	330	0.24	1490	720	298	0.1	479
05/13/04	36 Grand	CBFR	67 E	23.5	6.4	1.86	0.8	15	2.09	30	0.14	1340	230	29	0	79
05/13/04	36 Grand	CBFR	67 F	23.5	9.0	1.1	10	67	2.5	230	0.23	1500	660	324	0.1	510
01/09/03	36 Grand	ssR	5--1 B Rep	23.5	4.4	1.88	2	19	2.42	40	0.17	1370	280	49	0	116
01/09/03	37 College	OB	40-10	24.5	9.4	0.73	11	81	2.01	320	0.17	1180	640	280	0.1	630
01/09/03	37 College	OB	420-Oct	24.5	7.9	0.74	11	76	2.08	390	0.15	1455	570	331	0	574
01/09/03	37 College	OB	420-30	24.5	8.2	0.77	10	91	2.17	530	0.14	1315	590	401	0	681
01/09/03	37 College	OB	430-40	24.5	8.9	0.79	10	106	2.12	510	0.14	1255	630	468	0	620
01/09/03	37 College	OB	440-45	24.5	8.8	0.85	10	104	2.13	600	0.14	1510	620	499	0	600
01/09/03	37 College	CE	4 A	24.5	6.8	0.56	11	66	1.91	230	0.19	1545	530	200	0.1	491
01/09/03	37 College	CBF	4 B	24.5	8.2	0.67	11	79	2.04	310	0.22	1635	560	253	0.1	574
01/09/03	37 College	CE	4 C	24.5	5.3	0.29	9.1	46	1.38	110	0.13	386	310	134	0.1	412
01/11/03	38 Water St.	CB	8 A	25.6	6.4	0.56	11	56	1.45	190	0.2	396	470	134	0.1	561
01/11/03	38 Water St.	CBF	8 B	25.6	7.3	0.67	11	70	1.64	210	0.23	687	520	166	0.1	602
02/28/04	39 Hampton	CE	48 A	28.3	12.5	1.23	18	27	3.07	80	0.2	1640	630	214	<0.01	600
02/28/04	39 Hampton	CBF	48 B	28.3	13.0	1.42	13	43	1.86	90	0.29	1640	790	130	0.1	425
06/18/03	40 Lynn St.	CE	26 A	29.3	7.0	0.89	>15.0	24	2.26	60	0.28	1595	750	167	0.1	328
06/18/03	40 Lynn St.	CE	26 B	29.3	10.5	1.24	13	47	2.91	80	0.27	2500	800	164	0.1	330
06/18/03	41 NJ Glenstn.	CE	27 A	30.1	6.2	0.56	>15.0	65	2.16	40	0.61	448	520	180	<0.5	427
06/18/03	41 NJ Glenstn.	CBF	27 B	30.1	8.1	0.71	>15.0	43	2.61	50	0.47	637	510	209	<0.5	448

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca % ppm	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
01/11/03	42 Blaine	CB	7	31	11.0	1.58	6.4	30	2.27	60	0.16	1485	780	63	0.1	282
05/12/04 T-1	tS PP	tCB	60 A	8.85	8.5	1.13	0.9	25	1.5	230	0.1	1465	890	76	0	114
05/12/04 T-1	tS PP	tCB	60 B	8.85	7.1	1.23	0.6	32	1.68	310	0.11	1195	1220	63	0	142
05/12/04 T-2	tSE PP	tCE	61 A	10.7	9.3	1.23	1.4	34	2.14	80	0.15	1230	700	50	0.1	261
05/12/04 T-2	tSE PP	tCE	61 B	10.7	10.6	1.14	1.7	37	2.19	120	0.17	832	860	43	0.3	285
02/21/04 T-3	WWTP15	tCB	43	12.3	28.4	2.09	4.1	29	2.49	210	0.18	2100	740	85	0.1	207
02/21/04 T-4	WWTP16	tCB	44	12.3	8.1	2.09	4.5	19	2.9	140	0.15	3440	610	55	0.1	110
02/21/04 T-5	WWTP17	tCB	45	12.3	8.0	2.43	1.2	17	2.74	40	0.19	2280	490	38	0	78
02/21/04 T-6	WWTP18	tCB	46	12.3	8.1	2.08	3	21	2.28	50	0.21	2300	500	40	0	98
02/21/04 T-7	WWTP19	tCB	47	12.3	8.0	2.43	2.4	19	2.8	40	0.2	2510	640	41	0.1	102
01/23/03 T-8	South Ck	tCE	14 A	12.3	6.8	1.43	1.3	16	1.92	50	0.12	1750	600	30	0	88
01/23/03 T-8	South Ck	tCE	14 B	12.3	10.0	1.6	2.2	17	1.91	60	0.14	1635	660	28	0	102
01/23/03 T-8	South Ck	tCE	14 C	12.3	11.9	1.47	1.7	17	1.94	50	0.14	1840	710	31	0	100
06/18/03 T-9	Sunset Rd.	tCB	24 A	12.3	13.8	0.84	>15.0	25	1.34	40	0.36	930	880	146	<0.5	253
06/18/03 T-9	Sunset Rd.	tCBF	24 B	12.3	6.8	0.66	>15.0	36	1.73	10	0.53	502	490	186	<0.5	972
05/12/04 T-10	tNE PP	tCB	59 A	13.5	7.2	1.7	1	14	2.32	30	0.12	3190	510	56	0	89
05/12/04 T-10	tNE PP	tCB	59 B	13.5	14.2	1.48	1.8	14	1.88	50	0.12	1690	810	27	0.1	172
06/18/03 T-11	W. Grand	tCE	22 A	19.3	12.5	2.13	6.1	36	2.55	60	0.22	1490	850	100	0.1	797
06/18/03 T-11	W. Grand	tCBF	22 B	19.3	11.7	2.4	4.4	34	3.9	50	0.19	3520	820	102	0.1	807
01/09/03 T-12	Fassnight	OB	30-10	22	32.38	10.3	1.02	1.8	26	1.84	0.1	1330	560	123	0	156
01/09/03 T-12	Fassnight	OB	3 10--20	22	21.44	7.7	1	1.2	23	1.74	0.09	1395	440	122	0	140
01/09/03 T-12	Fassnight	OB	3 20-30	22	1.95	5.5	0.91	0.5	16	1.61	0.07	1230	320	51	0	78
01/09/03 T-12	Fassnight	OB	3 30-40	22	0.92	4.1	0.82	0.3	11	1.35	0.06	1080	260	33	0	35
01/09/03 T-12	Fassnight	OB	3 40-50	22	0.00	3.9	0.8	0.3	10	1.3	0.06	1020	220	22	0	27
01/09/03 T-12	Fassnight	OBAb	3 50-60	22	0.00	5.1	0.93	0.4	12	1.44	0.07	1105	300	23	0	34
01/09/03 T-12	Fassnight	OBAb	3 60-70	22	0.00	6.6	1.2	0.5	14	1.58	0.09	1245	350	23	0	46
01/09/03 T-12	Fassnight	OBAb	3 70-80	22	6.8	1.32	0.5	14	1.62	30	0.1	1205	330	23	0	48

Collect Date	Site # Name	Sample Type * #	Depth (cm)	Stream Cs ** (Km)	OM Bq/Kg %	Al %	Ca %	Cu ppm	Fe %	Hg ppb	Mg %	Mn ppm	P ppm	Pb ppm	S %	Zn ppm
01/09/03	T-12 Fassnight	OBAb	3 80-90	22	5.6	1.32	0.5	13	1.59	20	0.1	1090	230	23	0	46
01/09/03	T-12 Fassnight	OBAb	3 90-100	22	5.1	1.48	0.5	12	1.65	20	0.1	897	180	21	0	46
01/09/03	T-12 Fassnight	OBAb	3 100-110	22	5.7	1.46	0.5	12	1.9	20	0.1	705	200	25	0	47
01/09/03	T-12 Fassnight	OBAb	3 110-120	22	5.7	1.45	0.5	12	1.62	20	0.1	207	190	25	0	47
01/09/03	T-12 Fassnight	OBAb	3 120-130	22	4.4	1.51	0.5	13	1.59	20	0.1	210	190	27	0	48
01/09/03	T-12 Fassnight	OBAb	3 130-140	22	5.4	1.5	0.5	14	1.78	20	0.11	343	240	30	0	52
01/09/03	T-12 Fassnight	OBAb	3 150-160	22	5.3	1.86	0.5	16	2.98	20	0.16	3370	230	38	<0.01	71
01/09/03	T-12 Fassnight	OBAb	3 190-200	22	8.3	2.81	0.6	20	5.1	60	0.11	5530	320	57	0	96
01/09/03	T-12 Fassnight	tCE	3 A	22	9.9	1.56	3	23	2.56	100	0.15	2520	570	77	0	168
01/09/03	T-12 Fassnight	tCE	3 B	22	6.1	1.85	0.9	19	4.29	30	0.11	4430	400	64	0	96
01/09/03	T-12 Fassnight	tCBF	3 C	22	8.7	1.2	4.6	26	2.13	130	0.15	1570	500	180	0	220
06/18/03	T-13 Fn Grant	tCE	28 A	22	6.4	0.72	14	16	3.16	40	0.21	1720	660	205	0	301
06/18/03	T-13 Fn Grant	tCBF	28 B	22	9.9	1.08	12	28	3	70	0.24	1730	820	198	0.1	358
01/11/03	T-14 Phelps	CB	9 A	25.1	9.9	0.85	12	51	2.57	100	0.31	1175	730	182	0.1	720
01/11/03	T-14 Phelps	CBF	9 B	25.1	10.6	0.69	12	43	1.94	90	0.27	657	700	243	0.1	598
06/18/03	T-15 SJ Frmnt.	tCE	25 A	27.2	8.3	2.55	4	37	4.94	110	0.17	3440	800	148	0.1	481
06/18/03	T-15 SJ Frmnt.	tCBF	25 B	27.2	10.6	1.81	5.1	74	3.06	230	0.22	1110	730	207	0.1	1125
01/11/03	T-16 SJ Glenstn.	CE	6 A	27.2	8.8	1.82	8.5	69	2.38	150	0.26	872	1340	414	0.1	418
01/11/03	T-16 SJ Glenstn.	CBF	6 B	27.2	7.0	2.06	8.7	29	2.26	190	0.23	905	1340	351	0.1	356
05/13/04	S-1 SE PP	SPP	70	~10.9	14.5	1.27	0.5	35	1.64	450	0.1	1170	1300	53	0.1	134
05/13/04	S-2 SW PP	SPP	71	~8.85	9.6	0.82	0.4	16	1.3	190	0.08	1730	560	52	0	61
05/13/04	S-3 NW PP	SPP	73	~8.85	10.0	0.77	1.4	18	1.88	90	0.07	1100	780	38	0	52
05/13/04	S-4 NE PP	SPP	72	~13.5	10.5	1.33	0.6	19	1.53	240	0.08	818	740	39	0	89
05/13/04	S-5 Walnut	SI	65	~24.7	12.1	0.72	17	69	1.76	90	0.35	676	700	262	0.2	585
05/13/04	S-6 Main	SI	64	~26.2	5.9	0.31	18	25	1.14	40	0.19	310	330	96	<0.01	347
05/13/04	S-7 N. Jones	SI	63	~27.3	12.3	0.66	>25.0	343	1.98	170	0.43	607	830	235	<0.01	2140
05/13/04	S-8 Stewart	SI	62	~27.2	7.5	1.56	12	34	2.05	80	0.26	1340	740	91	0.1	273

Collect	Site	Sample	Depth	Stream	Cs **	OM	Al	Ca	Cu	Fe	Hg	Mg	Mn	P	Pb	S	Zn
Date	#	Name	Type * #	(cm)	(Km)	Bq/Kg	%	%	% ppm	%	ppb	%	ppm	ppm	ppm	%	ppm

* Sample Types - Channel bed (CB), Channel Edge (CE), Channel Bankfull (CBF), Channel Terrace (CT), Overbank with Hg above or equal to 50 ppb (OB), Overbank with Hg below 50 ppb (OBAb), Tributary Channel bed (tCB), Tributary Channel Edge (tCE), Tributary Channel Bankfull (tCBF), Tributary Overbank with Hg above or equal to 50 ppb (tOB), Tributary Overbank with Hg below 50 ppb (tOBAb), Watershed Surface Historic Industrial Area (SI), Watershed Surface Power Plant (SPP), Replicate (R), Sub-Sample Replicate (ssR)

** Cs samples were collected at a later date (4-24-03)