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Distribution of Trace Elements in Cumberland River Basin Reservoir Sediments

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DISTRIBUTION OF TRACE ELEMENTS IN
CUMBERLAND RIVER BASIN RESERVOIR SEDIMENTS

A Thesis
Presented to
The Faculty of the Department of Geography and Geology
Western Kentucky University
Bowling Green, Kentucky

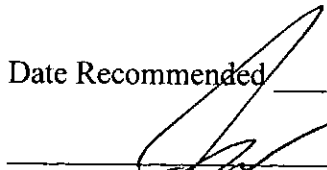
In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

By
Laura Mahoney Benneyworth

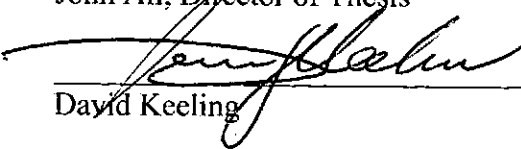
December 2011

**DISTRIBUTION OF TRACE ELEMENTS IN
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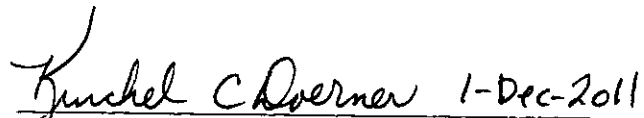
John All, Director of Thesis



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Laura Mahoney Benneyworth

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68 Pages

Directed by: John All, David Keeling, and Jun Yan

Department of Geography and Geology

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The U.S. Army Corps of Engineers, Nashville District, maintains ten reservoirs in the Cumberland River Basin in Kentucky and Tennessee, and has been monitoring sediment chemistry in the reservoirs since 1994. The purpose of this study is to evaluate the sediment data collected from the reservoirs from 1994 to 2010 to determine if there are any spatial patterns of the trace elements: arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, and zinc. The results indicated that trace element levels were consistent with national baseline concentrations measured by the U.S. Geological Survey. Center Hill reservoir had the greatest number of trace element concentrations (all except cadmium) that were significantly higher when compared to all other reservoirs. The degree of urbanization in the reservoir basins was based on population density from the 2000 Census and the percentage of developed land using the 2006 national land cover dataset. Aquatic toxicity values were used as a measure of sediment quality. The reservoirs with the worst aquatic toxicity rankings were not the most urban, instead they were the reservoirs with the longest retention times. Therefore, it may be concluded that retention time has a larger effect on Cumberland River Basin sediment concentrations than the type of land use or the degree of urbanization. The results also indicate that it may be prudent to include an evaluation of quality based on aquatic

toxicity when monitoring sediment quality, and that when reservoirs are the subject of sediment quality assessments, the consideration of the physical properties of the reservoir, especially the retention time, is essential for a comprehensive evaluation. This may also imply that sediment quality in reservoirs may effectively be regulated by water resource management techniques at the reservoirs that affect retention time.

CHAPTER ONE: INTRODUCTION

All life depends on less than one percent of the total quantity of water on the planet (Hornberger, et al., 1998). With projected increases in global human populations, the demand for water has become more critical than ever. Currently, more than 1 billion people worldwide lack access to safe drinking water, and water-related diseases lead to two to five million deaths annually (Gleick, 2003; Rijsberman, 2006). There are some areas in the world where water scarcity is not an issue; however, the spatial distribution of water supplies does not always coincide with human needs. If there is no mechanism to store excess water, it can be wasted; alternatively, if excess water is not controlled, flooding and possible loss of life and property may result. The construction of reservoirs is one way in which the control of water has historically been addressed (Rijsberman, 2006; WES, 1998).

With increased population comes an increased proportion of urbanized land. Increases in urbanized land result in higher levels of runoff from non-point sources; this subsequently can result in higher concentrations of contaminants in surrounding water bodies and sediments (Novotny and Olem, 1994). The characteristics of sediment contamination in a watershed have been reported to relate to land use activities (USEPA, 1997), as well as to the physical properties of the substrate and hydrological conditions of the watershed (Novotny and Olem, 1994).

One of the most important watersheds in the southeastern U. S. is the Cumberland River Basin (CRB), located in southern Kentucky and in northern Tennessee. The U.S. Army Corps of Engineers, Nashville District (USACE), has authority for, and maintains, ten reservoirs in the CRB. The USACE has been monitoring sediment chemistry in the

reservoirs since 1994. The purpose of this study is to evaluate the reservoir sediment quality data to determine if there are any spatial patterns of trace elements detected in the CRB sediments collected from 1994 to 2010. The trace elements evaluated include: arsenic (As); beryllium (Be); cadmium (Cd); chromium (Cr); copper (Cu); lead (Pb); mercury (Hg); nickel (Ni), and zinc (Zn).

Reservoirs play an important role in the management of water resources, and provide many functions such as flood control and water supply. Reservoirs can also act as “traps” for sediments originating from upstream watersheds. Previous sediment quality studies have been conducted on trace elements in lakes and reservoirs by a variety of organizations, most notably the U.S. Geological Survey (USGS) and the U.S. Environmental Protection Agency (USEPA). Most of these studies, however, have not been conducted on a watershed as large as the CRB, or the sediments monitored over a period of time as long as the USACE’s program.

Increased development of farmland and urbanization results in greater erosion and runoff, and increased areas of impervious surface. Urban sediments have been studied extensively over the past several decades. The types of contaminants commonly found in urban sediments include fertilizers, nutrients, pesticides, and trace elements (inorganics) including all of the elements of interest. Sources of trace elements in sediments are the result of natural processes such as erosion, but also include anthropogenic sources such as atmospheric deposition from combustion of fossil fuels and municipal wastes, industrial processes, rooftops, and agricultural runoff. Historically, urban sediment quality has been shown to be correlated to land use activities. However, more recent studies (Chalmers, et al., 2007; Horowitz and Stephens, 2008; USGS, 2009) indicate that

population density is a more important determinant in sediment quality than land use or upstream geology. The evaluation of sediment quality is important because non-point source pollution, which contributes significantly to sediment contamination, is the greatest source of impairment in the nation's water bodies. Furthermore, the presence of contaminants in sediments can potentially have effects on entire ecosystems.

The null hypothesis tested in this study is that there is no significant difference in the sediment quality in any of the USACE reservoirs. Because the reservoirs are spatially distributed over a large area (about 18,000 square miles), it is assumed that the trace element concentrations in sediment are independent from one another, as each reservoir would be associated with unique point and non-point sources. The research objectives of the study are to: 1) examine the range of concentrations of trace elements from each reservoir for patterns of contamination; 2) compare measured sediment concentrations from the USACE reservoirs to representative background concentrations; 3) compare the entire database of trace element concentrations from all reservoirs collectively to each individual reservoir to determine if the concentrations were significantly different from one another; 4) evaluate any trends in sediment concentrations over time; 5) compare the measured sediment concentrations to relevant benchmarks to assess sediment quality and toxicity; and 6) determine if there is any correlation with the degree of "urbanization" of the reservoir watersheds with the measured trace element sediment concentrations.

The research objectives were accomplished by use of a variety of geospatial analyses, including data exploration and visualization, geographic information systems (GIS), and statistics. All of the sediment data were collected by the USACE prior to data analysis. Relevant hydrologic properties of the CRB reservoirs were compiled and

evaluated. Land cover was evaluated using the national 2006 dataset. The relative “urban rank” of each reservoir was estimated by population density using 2000 census data. Trends in sediment quality in the reservoirs were evaluated by use of box and whisker plots, Excel plots, nonparametric two-sided hypothesis tests, and outlier tests. Concentrations of trace elements were compared to representative background levels generated by the USGS, and the potential for aquatic toxicity was evaluated by comparison to established sediment quality criteria.

By evaluating the distribution of sediment concentrations of trace elements in the USACE’s CRB reservoirs, the role of hydrology and urbanization on sediment contamination was investigated, and potential sources impacting the reservoir sediments were evaluated. For the CRB sediments, hydrology, particularly retention time, was found to have a greater bearing on sediment concentrations than the degree of urbanization of the watershed. This finding may have an impact on the future assessments of reservoir sediment quality, and on best management practices for urban non-point source pollution.

CHAPTER TWO: BACKGROUND

Physical geography is an integrative science that seeks to explain and predict the spatial distribution of human activity on physical features on the earth. Geographers study how and why things differ from place to place, and the change in patterns over time. Geography is a “problem-solving discipline” (McGrew and Monroe, 2000). The term “geospatial” is often used to refer to a location relative to the Earth's surface (de Smith, et al., 2006). However, geospatial *analysis* has been described as a process for looking at geographic patterns and relationships between features and processes (de Smith, et al., 2006), and can include many contexts where the evaluation of space is important in terms of what happens and where. Some common types of geospatial analyses include: mapping where things are located; evaluating the most and least of something; mapping the density of entities and phenomena; finding what is nearby; finding what is inside; and evaluating change through time and space (Mitchell, 1999). Specifically, geospatial analysis may employ data mining and exploration, database design and development, surface analysis, image interpretation, data analysis, statistics, modeling, and data visualization. It may involve the use of GIS, or it may not involve a graphic representation or map of the information at all. As described by de Smith, et al. (2006), geospatial data analysis assists in understanding both first order (environmental) effects, and second-order (interaction) effects. Analytical approaches may be data-driven, involving the exploration of geospatial data; model-driven, involving testing hypotheses and creating models; or both. The evaluation of the distribution and nature of pollutants in the environment is, at its very essence, the study of spatial distribution of human

activity on physical features on the earth; therefore, geospatial analysis is integral and implicit in the process.

Geospatial analysis was used to evaluate the interaction of non-point source pollution and sediment chemistry in the CRB reservoirs. Background information is first given regarding:

- the importance of lakes and reservoirs,
- comparison of lake and reservoir characteristics,
- sources of trace elements in sediment,
- sediment quality,
- sediment monitoring,
- urban sediments, and
- measures of urbanization

Importance of Lakes, Reservoirs, and Dams

Reservoirs are constructed to address specific water needs, including municipal and drinking water supplies, agricultural irrigation, industrial and cooling water supplies, power generation, flood control, sport or commercial fisheries, recreation, aesthetics, and navigation. It has been estimated that approximately 25 percent of all water previously flowing to the oceans is now impounded in reservoirs (UNEP, 2000).

Reservoirs represent an important component of the socioeconomic structure of both developed and developing countries. Nearly all major river systems in the world have reservoirs in their drainage basins, and reservoirs exist on all continents and in all countries (except Antarctica), although their distribution within regions is irregular. Most reservoirs are concentrated in the temperate and sub-tropical zones of the northern and

southern hemisphere. More than half of the world's reservoirs are located in the U.S, Canada, Mexico, Brazil, China, and India (UNEP, 2000).

The first reservoirs were thought to have been constructed about 4,000 years ago in China, Egypt, and Mesopotamia for drinking water and irrigation. The total volume of globally impounded water has increased about 12 times after World War II, including a 40-fold increase in Latin America and a 100-fold increase in Africa and Asia. The building of reservoirs peaked in the late 1960s, and there has been essentially no new reservoir construction since then in North America and Europe. Most of the new reservoirs scheduled to come into operation in the 21st century are located in Asia, Africa, and Latin America (UNEP, 1999).

Lakes are used for many of the same purposes as reservoirs; however, most lakes are naturally formed, whereas reservoirs are built by humans, either by damming a flowing river or by diverting water from a river to an artificial basin (impoundment). Upon completion of a dam, the river pools behind the dam and fills the artificially created basin (WES, 1998). Several types of dams are constructed to make reservoirs. Small dams (3-6 meters above the natural river bed) may be used to store water for drinking purposes or to divert water flow of smaller rivers for various purposes, including the operation of mill water wheels. The most common type of dam is earth-filled; about 85 percent of the dams of heights between 15-60 meters are of this type. Arched dams are usually constructed where high dam walls are required, and account for 40-50 percent of the very large dams (dam height of 150 meters or more) around the world. An estimated 800,000 dams were in operation worldwide in 1997, and about 45,000 of these were large dams (UNEP, 2000).

Gleick (2003) calls the reliance of dams, reservoirs, aqueducts, pipelines for water management the “hard path”, where water resources are controlled through supply side solutions such as infrastructure, rather than the management of water from the demand side, by societal and economic control. All dam/reservoir construction projects have both beneficial and adverse environmental and socio-economic impacts. Benefits include improvement of local economies, improved energy supply, relief from flooding and droughts, supply of drinking water, and management of the world’s water resources. Negative aspects of the “hard path” have also included substantial and often unanticipated social, environmental, cultural, and economic impacts (Gleick, 2003). For example, the Aswan High Dam in Egypt (and Sudan), which impounds the Nile River, has resulted in the creation of over a million acres of arable land, protection from high floods and droughts, generation of hydroelectric power, and improved navigation possibilities. The Aswan High Dam, however, has also resulted in increased riverbank erosion, scouring, river meandering, decreased water quality due to increased industrial and agricultural discharges, increased reservoir siltation and eutrophication, increased water-vector related illnesses, and inundation of historical monuments (UNEP, 2000). Likewise, the Three Gorges Dam project in China was a monumental engineering accomplishment, but it has also displaced more than one million people whose villages were flooded by the reservoir behind it (Gleick, 2003).

Comparison of Lake and Reservoir Characteristics

In the U.S., reservoirs are generally located in areas where water demand is high, or flooding is frequent; reservoirs are rarely constructed where there is an abundance of natural lakes (WES, 1998). Natural lakes are generally circular, bowl-shaped, depressions in the land surface. The center of the lake is usually the deepest part, and the

lake usually has one inflowing and outflowing river channel. In contrast, reservoir basins usually have multiple tributary inputs, and are more irregular and dendritic in shape, with the “arms” radiating outward from the main body of the reservoir. The depth of a reservoir increases from the upstream end to the dam end of the water basin. The dendritic shape of many reservoirs provides a much longer shoreline than in lakes of similar volume. Reservoirs usually have larger drainage basins than lakes, and also have larger drainage-area-to-surface ratios (WES, 1998).

Many of the early reservoir studies focused on sediment loading from drainage basins because of eutrophication or siltation concerns. Sedimentation studies are important because the rate at which a reservoir filled with sediment is a major determinant of its useful operational life. Eutrophication is the enrichment of surface water bodies due to the presence of organic compounds originating from urban, agricultural, and industrial activities. If unchecked, eutrophication ultimately will reduce oxygen in the water column, killing fish and other organisms, and reducing biodiversity. Compared to lakes, reservoirs are more sustainable against the growing biological load due to the larger share of mineral particles in the sediments from abrasion of the shore (WES, 1998).

Compared to flowing streams, reservoirs are especially susceptible to sediment pollution due to their long retention times, complex responses to pollution inputs, and integrating nature (Moltz, et al., 2011). Water at the dam end of a reservoir is typically of higher quality than water entering the reservoir; and this can result in physical, chemical, and biological water quality gradients. However, because of large water inflows, flushing of contaminants may occur rapidly in reservoirs, unlike naturally-formed lakes.

Because of their larger drainage basins, and their multiple tributary inputs, the inflow of water into reservoirs is more directly tied to precipitation events in the drainage basin than it is in lakes (UNEP, 2000).

Sources of Trace Elements in Sediment

Trace element concentrations found in reservoir and lake sediments may enter the hydrologic cycle naturally, due to geological weathering processes and erosion during precipitation events, and/or may result from anthropogenic sources. In the absence of human inputs, lake and reservoir sediments usually result from erosion of bedrock and shorelines. As noted by Chapman, et al. (2003), naturally-occurring or "background" concentrations of trace elements in sediments vary greatly.

Reservoirs can act as sediment traps. As water enters a reservoir, the velocity of water is reduced, and sediment and other materials carried in the faster-flowing water will settle out, causing sedimentation (Ongley, 1996). Chemical accumulation in lake and reservoir sediment results mainly from the deposition of the elements adsorbed onto suspended particulate matter, as well as from the diffusion of dissolved concentrations from the overlying water column (Chapman, et al., 2003; Ongley, 1996).

Sediment texture, particle size, and particulate organic matter can be very important to the fate and transport of some elements in streams and lakes (Paul and Meyer, 2001). Coarser material is deposited rapidly at the point where the water body enters the reservoir, and is only redistributed under highly turbulent conditions. Fine material is suspended, and may be repeatedly resuspended by rain, wind, and lake currents until it eventually settles out in depositional areas (Ongley, 1996). In many rivers 50 to 100 percent of the suspended load will be composed only of silt+clay sized

particles less than 0.62 μm ; it is this sediment fraction that is mainly responsible for the transport of chemicals adsorbed on particles (Ongley, 1996).

Some trace elements, because of their geochemical properties, can be remobilized after being deposited in sediments. Fine-grained sediments in floodplain deposits are stored for long periods, and can be remobilized many years later by bank erosion during floods or by geochemical weathering and leaching, often enhanced by increased acidity (Novotny and Olem, 1994). Recently deposited trace elements in soft sediments can provide information on transport processes and sources (Chapman, et al., 2003). As deposition occurs over time, deep sediments in lakes and reservoirs can become a historical record of the temporal trends of chemicals in the environment (Ongley, 1996).

Anthropogenic sources of sediment contaminants consist of point sources and non-point sources. Point sources, such as industrial effluents and municipal wastewater discharges to water bodies are relatively easy to identify and isolate (USEPA, 2005). In contrast, non-point sources like stormwater, agricultural runoff, snowmelt, and atmospheric deposition of stack emissions are closely tied to precipitation and runoff events, are less predictable, more variable, and more difficult to identify than point sources (USEPA, 2005). In particular, the residence time of elemental mercury in the atmosphere from stack emissions (which may be deposited into water bodies) may be as much as one year, allowing its distribution over large distances, both regionally and globally (USEPA, 1997). Typically, non-point sources of trace elements are more important than point sources in urban streams (Paul and Meyer, 2001).

Sediment Quality

The management of freshwater ecosystems has historically focused on water quality. While initiatives undertaken in the past twenty years have improved water

quality conditions, evidence suggests that management efforts directed only at the improvement of surface water quality, rather than sediment quality, may not adequately protect the entire ecosystem.

Section 402 of the Clean Water Act (CWA) provides authority for issuing National Pollutant Discharge Elimination System (NPDES) permits for point discharges to the nation's water bodies (Percival, et al., 2009). The 1987 Water Quality Act Amendments to the CWA added Section 319, which established a national program to control non-point stormwater source pollution. Under section 305(b)(1)(A) of the CWA, states are required to submit reports on the quality of their waters to the USEPA every two years, and USEPA prepares a national report summarizing its findings on the quality of the nation's water resources. Under section 303(d) of the CWA, states are required to compile a list of impaired waters that fail to meet any of their applicable water quality standards or cannot support their designated or existing uses after imposition of technology based controls. This list, called a "303(d) list," is submitted to Congress every two years, and states are required to develop a Total Maximum Daily Load (TMDL) for each pollutant causing impairment of water bodies on the list. The TMDL provides waste load allocations for point source discharges; it is the sum of the loading from point sources as well as non-point sources, plus a margin of safety. The USEPA has developed the Assessment TMDL Tracking And Implementation System (ATTAINS) database and website to combine two formerly separate databases, the National Assessment Database (for 305(b)) and the TMDL Tracking System (for 303(d)) (USEPA, 2005). In addition, Section 314 of the Clean Lakes Program has awarded grants for the study and restoration of publicly owned lakes.

The USEPA (2011a) has estimated that the current water quality in 69 percent of the nation's 41.7 million acres of lakes, ponds, and reservoirs is "impaired" (with only about 46 percent of the nation's lakes assessed), based on data collected by states under the CWA 305(b) and 303(d) reporting requirements. The primary source of impairment nationally in lakes/reservoirs has changed over the last decade from agriculture to atmospheric deposition. As of 2011, the top sources of pollutants nationally to lakes, ponds, and reservoirs, in order, are: atmospheric deposition, "unknown/ unspecified sources", agriculture, natural/wildlife, hydromodification, "other", urban runoff/stormwater, municipal discharges/sewage, and unspecified nonpoint sources (USEPA, 2011a). Mercury, nutrients, polychlorinated biphenyls (PCBs), organic enrichment, and metals (other than mercury) were cited by USEPA as the current leading causes of impairment nationally in lakes/reservoirs. Mercury impairment was primarily due to mercury in fish tissue. Sedimentation was also listed as one of the top ten causes of impairment in lakes/reservoirs. Of impairment causes for the non-mercury metals, lead comprised about 60 percent. The most impaired designated use is currently "aquatic life harvesting" (74 percent impaired) (USEPA, 2011a). In 2000, the leading cause of impairment in lakes/reservoirs was nutrients (50 percent of impaired lake acres); agriculture was the leading source of impairment. Metals were reported as the second greatest cause of impairment in 2000 (42 percent of impaired lake acres); however, mercury was not listed separately from metals in the 2000 survey (USEPA, 2002). In Kentucky, as of 2010, mercury was listed as the primary cause of impairment in lakes, reservoirs and ponds, and atmospheric deposition was the primary source of impairment. In Tennessee, as of 2010, the primary causes of impairment to lakes, reservoirs and

ponds, was PCBs, followed by mercury, and the primary source of impairment was legacy pollutants, followed by atmospheric deposition (USEPA, 2011a).

Sediment pollution has two dimensions: (1) as a physical contaminant, from land degradation, erosion, and top soil loss, which can lead to excess turbidity in receiving streams, ecological impacts, and decreased storage capacity in reservoirs due to siltation; and (2) as a chemical contaminant, as a result of metals, pesticides, nutrients adsorbing to silt and clay fractions of the sediment. Chemical pollution is tied to both the particle size of the sediment, and the amount of particulate organic matter associated with the sediment (Novotny and Olem, 1994).

Contaminated sediments can have a critical effect on the overall health of an ecosystem and watershed (USEPA, 2004). Due to their physical and chemical properties many chemicals, including pesticides and metals found only in trace amounts in water, can bioaccumulate to elevated levels in sediments and biota (MacDonald and Ingersoll, 2002). Contaminated sediments can directly impact aquatic organisms, and represent a continuing source of potentially toxic substances that may also impact fish, wildlife, and humans through food or water consumption. Fish consumption advisories have resulted from sediment contamination in lakes, and have adversely affected commercial, sport, and food fisheries. The presence of mercury in fish tissues has resulted in many fish advisories (USEPA, 1997). Ecological impacts are often evident in fish and other biota collected from contaminated sediment areas, including higher incidences of tumors and other abnormalities. Contaminated sediments can also have an impact on navigation. Approximately 300 million cubic yards of sediments are dredged from harbors and

shipping channels annually to maintain commerce and, of this amount, 3 to 12 million cubic yards require special handling and disposal (USEPA, 1997).

Sediment Monitoring

Reservoirs and freshwater lakes provide the US with 70 percent of its drinking water, and supply water for electric utilities, industry, and agriculture, as well as support the nation's 19-billion dollar freshwater fishing industry. Lakes and reservoirs also support complex ecosystems, and provide habitat for numerous threatened and endangered species (USEPA, 2009a). Therefore, monitoring the quality of these resources is an issue of national interest.

Although a number of organizations have monitored the sediments in lakes and reservoirs at various locations in the U.S., there are few published studies in the U.S. where sediments have been monitored in an entire basin over a decade or more. The USEPA conducted a series of lake surveys under the National Aquatic Resource Surveys (NARS) program in 2007, in which biological, recreational, chemical, and physical stressors on the nation's lakes were evaluated. Of the chemical stressors, mercury was the only trace element analyzed in sediments; however, these data were not available in the latest *National Lakes Assessment Report* (USEPA, 2009a).

The most comprehensive study of trace elements in sediments, to date, is the USGS's (2011) National Water Quality Assessment (NAWQA) program. Nationwide, from 1992 to 2002, the USGS sampled surface water and bed sediments from 51 river basins, representing a variety of land-use types, resulting in over 1,000 samples that were field sieved to yield total concentrations. Sampling was done in the summer or autumn low flow to minimize seasonal variability, samples were composited, and locations were limited to depositional zones. None of the NAWQA sampling locations were located in

Kentucky, or in the CRB in Tennessee. Baseline trace element sediment concentrations for the entire U.S. were generated in the NAWQA program; these represented concentrations for 448 sites that were predominantly undeveloped and non-urban, and thus can be viewed to represent national, representative “background” concentrations (Horowitz and Stephens, 2008).

Urban Sediments

The types of contaminants found in reservoir sediments can reveal much about the surrounding land use and types of development that have occurred in a watershed (USEPA, 1997) (Table 1). Urban settings are often associated with sediment contamination due to the presence of industrial and municipal discharges and emissions, contaminated runoff, and the widespread use of motor vehicles (Callendar and Rice; 2000; Van Metre and Mahler, 2003; 2004). Rice (1999) found that the anthropogenic sources contributing most to the presence of trace elements in water bodies were: combustion of fossil fuels in power plants; combustion of municipal solid waste; metal smelters; automobile emissions and wear of automobile parts; biomass burning; direct discharges from industrial sources and municipal sewage sludge; acid mine drainage; and runoff of manure and artificial fertilizers from farms. All of the trace elements of interest to this study are found in coal, or are waste products from coal mining or coal combustion byproducts such as stack gas, fly ash, and coal sludge (USDOE, 1996; USEPA, 2009b).

The USEPA (2005) has noted that “street dirt” can have elevated concentrations of Cd, Cr, Cu, Pb, and Zn. Other studies have shown that correlations exist between Pb and Zn sediment concentrations, population, and traffic density (Callendar and Rice, 2000). Most of the lead in sediments is likely present from the pre-1973 use of leaded

gasoline; concentrations have steadily declined in sediments since the 1980s. Zinc concentrations have increased in urban areas with high traffic density over the past 50 years, roughly coinciding with increased urbanization in various watersheds studied (Councell, et al., 2004).

Table 1. Potential Sources of Elements Commonly Found in Urban Sediments^a

Chemical	Sources and Uses of Trace Elements in the Environment
Arsenic (As)	coal combustion, ore smelting, pig and poultry sewage, phosphate fertilizers, insecticides, fungicides; herbicide, metal roofing
Beryllium (Be)	coal combustion, nuclear weapons and reactors, aircraft and space vehicle structures, x-ray machines, mirrors, specialty ceramics, automobiles, computers, sports equipment
Cadmium (Cd)	coal combustion, smelters, iron and steel mills, electroplating, zinc ore, fertilizers, tire wear and exhaust, sewage sludge and wastewater, waste incineration, paint pigments, metal roofing, “street dirt”
Chromium (Cr)	steel works, electroplating, copper smelting, combustion of natural gas, oil and coal, sewage sludge, waste incineration, phosphate fertilizers, brake linings, tires, engine parts, “street dirt”
Copper (Cu)	copper mining and smelting, other non-ferrous smelters, plastic industry, steel works, agriculture, sewage sludge, plumbing, brake linings, tires, engine parts, “street dirt”
Lead (Pb)	leaded gasoline, paint, plastics, ceramics, asphalt shingles, brake linings, tires
Mercury (Hg)	coal combustion, municipal waste, commercial/industrial combustion, medical waste incinerators; production of chlorine and caustic soda (by mercury cell chlor-alkali plants); fluorescent lamps, wiring devices and switches (thermostats), mercuric oxide batteries, amalgamation, pulp and paper mills; cement manufacturing, wood processing (as an anti-fungal agent), use as a solvent for reactive and precious metals, preservative for pharmaceutical products
Nickel (Ni)	metal alloys, stainless steel, heat exchangers, valves, brake linings, tires, engine parts, plating, batteries, coloring ceramics
Zinc (Zn)	zinc smelters, metal mining and production, coal combustion, waste incineration, wastewater sewage sludge, phosphate fertilizer, galvanized metal, deicing salts, tires and brakes, “street dirt”

^aSources: Rice, 1999; USEPA, 2004; Councell, et al., 2004; Paul and Meyer, 2001; USEPA, 2005; ATSDR, 2011.

The contribution of particles from rooftops to contaminant loading in urban streams on a watershed scale was studied by Van Meter and Mahler (2003). They found that metal roofing was a source of Cd and Zn, and asphalt shingles were a source of Pb. Van Meter and Mahler (2003) also reported that the range of trace element contributions from rooftop washoff to watershed loading was 6 percent for As and Cr to 55 percent for Zn. The greatest contribution of trace metals from atmospheric deposition of particles onto rooftops was for Hg (46 percent). Brigham, et al. (2003) reported that the source of more than 85 percent of the inorganic Hg in the atmosphere is coal-fired facilities and industrial boilers. As noted previously, the USEPA has estimated that Hg is currently the greatest cause of impairment of the nation's lakes and reservoirs, and atmospheric deposition was the greatest source of impairment (USEPA, 2009c).

Measures of Urbanization

It follows that if increased anthropogenic activities mean higher concentrations of trace elements in sediments, then increased urbanization means greater anthropogenic activities. The US Census Bureau defines "urban" for the 2000 Census as all territory, population, and housing units located in an urbanized area or an urban cluster (US Census Bureau, 2011). An "urbanized area" is defined as a densely settled territory that contains 50,000 or more people, and an "urban cluster" is defined as densely settled territory that contains at least 2,500 people, but fewer than 50,000 people (US Census Bureau, 2002). "Densely settled territory" consists of census blocks or block groups that have a population density of 1,000 people/ square mile or more, and surrounding census blocks that have an overall density of at least 500 people/square mile. "Rural" is defined as areas outside of urbanized areas and urban clusters (US Census Bureau, 2011).

Roy, et al. (2009) used road, sewer, and septic density, and percent urban, percent impervious surface, and percent agriculture, as measures of anthropogenic disturbance to water quality. Chalmers, et al. (2007) correlated urbanization and sediment metal concentrations using percent urban, CIT (commercial, industrial, and transportation), and residential land use. Chalmers et al. (2007) used population density as indicators of urbanization; “urban” was defined as CIT land use of greater than 20 percent. Brown, et al. (2009) used three variables to describe urban intensity in a study of the impacts of urbanization on stream ecosystems in metropolitan areas: housing density, percent developed land in the basin, and road density; water quality was measured, but sediment quality was not.

Horowitz and Stephens (2008) evaluated the role of land use, upstream geology, and population density on trace element sediment concentrations from the NAWQA program. Of the land use types evaluated (agriculture, urban, undeveloped, and mixed), they found that the only land use that affected sediment chemistry was urban, based on the 1992 National Land Cover Dataset (NLCD). Horowitz and Stephens (2008) concluded that population density (based on the 2000 Census) had a more consistent effect on sediment chemistry than either land use or upstream geology, but they qualified that the results may partially be a function of scale and sampling design.

The USGS (2009) studied nine metropolitan areas as part of the NAWQA program to develop a nationally consistent metric for urban intensity. Over 90 demographic, land cover, and infrastructure variables were evaluated. Population density based on census blocks (2000 census) was chosen as the central determinant of urban

intensity in the USGS studies, because urban effects are associated with goods and services with an increasing population.

The amount of impervious surface has been studied frequently as a surrogate for urban intensity (USEPA, 2005). In areas with high population density, high levels of impervious surface are inferred. Although all of these studies made thorough evaluations of land use, population density, and sediment concentrations, none published accompanying hydrologic information about the water bodies from which the samples were collected, so it is not possible to determine how hydrology may have affected measured sediment concentrations.

CHAPTER THREE: MATERIALS AND METHODS

Hydrology

The CRB includes over 7,500 square miles in Kentucky and over 10,000 square miles in Tennessee (Figure 1). The basin is approximately 350 miles long, and averages 50 miles wide. The USACE maintains ten reservoirs in the CRB that provide a variety of services, including hydropower, navigation, flood control, recreation, and water supply. Land use in the vicinity of the reservoirs varies considerable with the local communities, but includes industrial, commercial, residential, manufacturing, retail, and agriculture (USACE, 1996).

At its source, the Cumberland River and its tributaries flow in very deep, steep-sided valleys through rugged terrain. Elevations in the basin range from 4,150 feet in the eastern headwaters to 302 feet at the Ohio River confluence east of Lake Barkley. The Cumberland River is formed by two tributaries that each contribute only one percent of the total CRB flow: the Clover Fork, and the Poor Fork, located downstream of Harlan, Kentucky. The largest major tributary is the Caney Fork, which contributes 15 percent of the total CRB flow (USACE, 1996).

Main stem dam projects are located on major waterways, and have control capabilities, as opposed to a tributary dam; main stem dams include run-of-the-river dams. A run-of-the-river dam has a limited storage, low hydraulic head, and no positive control over water storage; discharge is a function of inflow. Storage dams are deep, typically more than 100 feet, and have maximum hydraulic head, which provides for

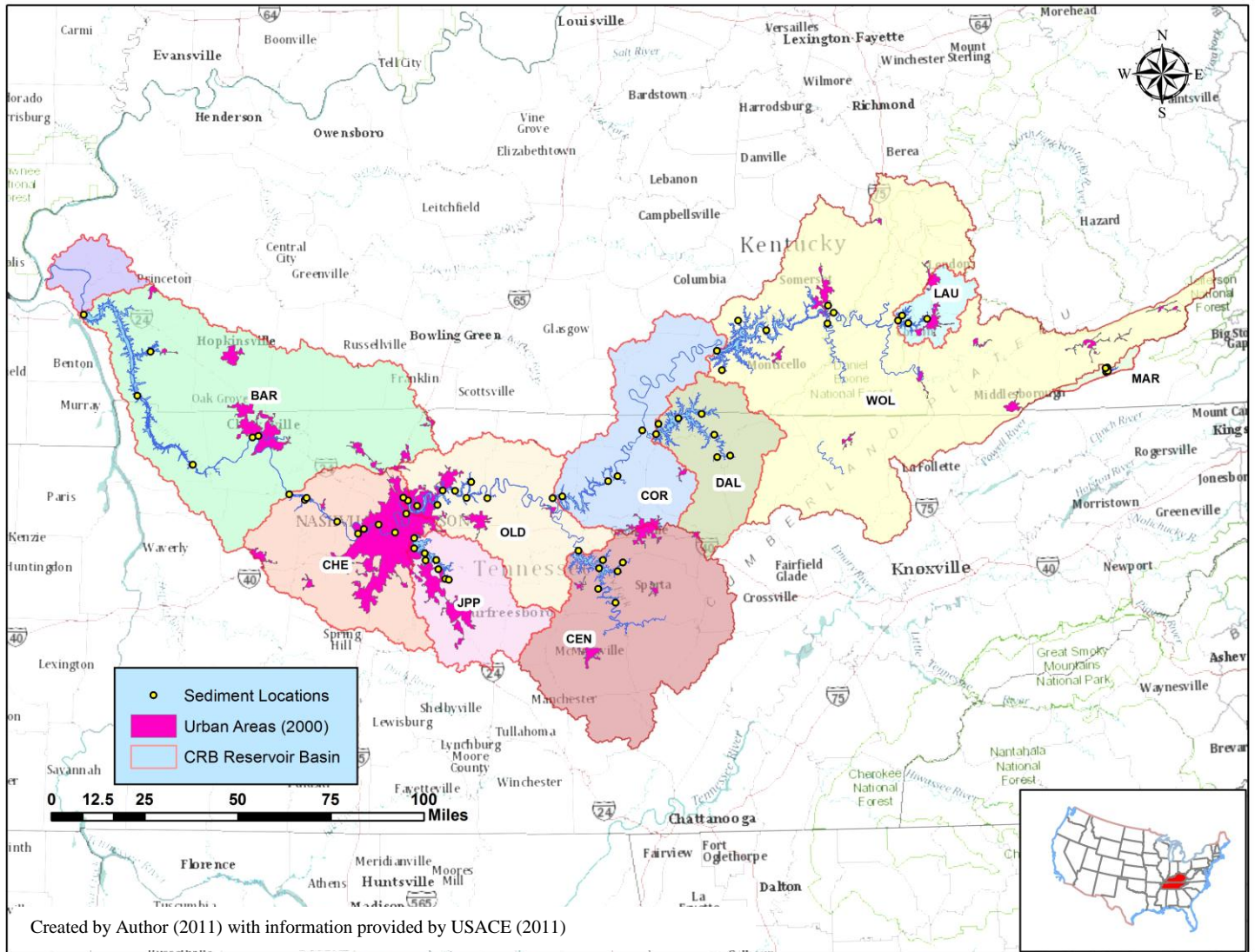


Figure 1. Location of CRB Reservoirs

hydropower generation, and storage capabilities that provide for flood control (WES, 1998). Five of the ten USACE reservoirs in the CRB are located on the Cumberland River (i.e., main stem, noted by an asterisk, *), and five are located on its tributaries.

The USACE reservoirs, in hydrologic order, include: Martin's Fork, Laurel River, *Wolf Creek/Lake Cumberland, Dale Hollow, *Cordell Hull, Center Hill, *Old Hickory, J. Percy Priest, *Cheatham, and *Lake Barkley. The Lower Cumberland is shown in Figure 1 north of Lake Barkley, but it is not part of the Upper CRB. The drainage basins generally correspond to the eight digit HUC (Hydrologic Unit Codes). All of the reservoirs except Martin's Fork produce hydropower. Four reservoirs (*Barkley, *Cheatham, *Old Hickory, *Cordell Hull) have navigation locks, and five act as storage reservoirs (Center Hill, Dale Hollow, Laurel, *Wolf Creek/Lake Cumberland, J. Percy Priest and, to a lesser extent, Martin's Fork) (Table 2). The impound dates of the reservoirs range from 1944 to 1978 (USACE, 1996).

The total drainage area of the CRB is over 18,000 square miles, with Martin's Fork being the smallest at about 56 square miles, and Wolf Creek/Lake Cumberland having the largest local drainage area at over 5,400 square miles (USACE, 1996). The total (summer) flood storage of the ten CRB reservoirs is over 14 million acre-feet, with Wolf Creek/Lake Cumberland by far having the greatest capacity, at over 6 million acre-feet, providing 42 percent of the flood storage of the entire CRB (Table 3). This storage has been reduced somewhat with the lowering of the pool at Wolf Creek/Lake Cumberland associated with the rehab of the dam in recent years (USACE, 2010). Lake

Table 2. Summary of CRB Reservoir Functions

Reservoir	Abbreviation	River	Reservoir Functions						
			F	R	WQ	F/W	WS	N	H
Lake Barkley	*BAR	Cumberland	✓	✓	✓	✓	✓	✓	✓
Center Hill	CEN	Caney Fork	✓	✓	✓	✓	✓		✓
Cordell Hull	*COR	Cumberland		✓	✓	✓	✓	✓	✓
Dale Hollow	DAL	Obey	✓	✓	✓	✓	✓		✓
Laurel	LAU	Laurel		✓	✓	✓	✓		✓
Martin's Fork	MAR	Martin's Fork	✓	✓	✓	✓			
Wolf Creek/Lake Cumberland	*WOL	Cumberland	✓	✓	✓	✓	✓		✓
Cheatham	*CHE	Cumberland		✓	✓	✓	✓	✓	✓
J. Percy Priest	JPP	Stones	✓	✓	✓	✓	✓		✓
Old Hickory	*OLD	Cumberland		✓	✓	✓	✓	✓	✓

* Main stem reservoir.

Functions: F= flood control; R=recreational; WQ= water quality; F/W= fish and wildlife; WS=water supply;

N= navigation; H=hydropower.

Source: USACE (1996).

Table 3. Summary of Reservoir Properties^a

Reservoir	Years Sampled (1994-2010)	No. of Sediment Sample Locations ^b	Range of Depths Sampled (feet)	Reservoir Area (square mile)	Local Drainage Area (square mile)	DA:RA Ratio	DA:RA Ratio Rank	Retention Time (days) ^c	Reservoir Population Density (people/square mile) ^d	Urban Rank
*BAR	97, 02, 07	6	12 to 66	146	3,438	24	9	9	81	5
CEN	96, 01, 06	7	50 to 161	36	2,174	60	4	131	57	6
*COR	95, 00, 05, 10	5	6 to 70	21.8	1,372	63	2	8	32	8
DAL	95, 00, 05, 10	7	10 to 135	48.4	935	19	10	343	19	9
LAU	98, 03, 08	4	22 to 245	9.5	282	30	7	471	102	3
MAR	97, 02, 07	4	4 to 35	0.9	56	62	3	21	7	10
*WOL	98, 03, 08	7	9 to 160	99.2	5,451	55	5	140	49	7
*CHE	94, 99, 04, 09	11	3 to 40	11.6	1,594	137	1	2	380	1
JPP	94, 99, 04, 09	11	13 to 96	35.5	892	25	8	95	170	2
*OLD	96, 01, 06	8	8 to 71	42.9	1,404	33	6	11	97	4

* Main stem reservoir.

^aSource: USACE (1996); Tippit and Campbell (2011).

^bSample locations and number of samples varied slightly over the years, due to various reasons (Tippit and M. Campbell, 2011).

^cSource: Based on mean discharge and reservoir storage at typical minimum headwater elevation (Sneed 2006; 2011).

^dSource: Estimated in GIS from the 2000 US Census shapefiles ESRI (2008).

Barkley is the most downstream reservoir in the CRB, and it controls runoff from nearly 98 percent of the entire basin. In addition to being the only flood control dam in the CRB that also serves as a navigation pool, Lake Barkley is unique because it is connected by a canal to Kentucky Lake, a TVA lake. The area between Lake Barkley and Kentucky Lake is called “The Land Between the Lakes”, and is managed by the U.S. Department of the Interior, Forest Service (USACE, 1996).

On May 1-2, 2010, the CRB experienced what has been characterized as a large-scale, regional flash flood, estimated at “greater than a 1,000 year storm” (USACE, 2010). This historic rainfall event resulted in severe flooding on the Cumberland and lower Tennessee Rivers in northern Tennessee and southwestern Kentucky. The precipitation was very intense, and produced record rainfall, stage, and discharge amounts across the CRB. Rainfall amounts exceeded 17 inches during the two-day event for some areas, the highest amount in more than 140 years of record. Much of the rain fell in areas not controlled by the USACE reservoirs. The full storage capacity of Wolf Creek, Dale Hollow, and Center Hill dams was unable to be used because the rainfall was concentrated in drainage areas downstream of the dams. Just upstream of Nashville, the J. Percy Priest dam’s flood storage capacity was exceeded, which required opening of the spillway gates to avoid overtopping. Spillway gate operations were required at both Cordell Hull and Old Hickory to prevent overtopping and losing control of water releases, and the Cheatham dam was overtopped (USACE, 2010). It is unknown what impact the flood has had on the CRB sediments, but it is reasonable to assume that sediments in affected reservoirs would be disturbed and likely transported downstream.

The two reservoirs that were sampled in 2010 by the USACE after the flood were Dale Hollow and Cordell Hull; Dale Hollow was not affected by the flood.

The average length of time it takes for water to flush out of a reservoir is its retention time, which is generally determined by the reservoir's water source, size, inflow/outflow regime, and watershed size. Retention time is estimated by the storage capacity (acre-feet) divided by the annual runoff (feet/year). Main stem dams usually have short retention times, and are more shallow than storage dams, which generally have long retention times (WES, 1998).

Hydraulic retention times in the CRB reservoirs range dramatically, from very short (2 days in Cheatham) to over a year (471 days) in Laurel (see Table 3). Local drainage basin area to reservoir area (DA: RA) ratios were estimated for each reservoir and ranked (1 highest). The reservoirs with the shortest retention times and the largest local drainage areas were main stem reservoirs (shown with an asterisk,*). The top two CRB reservoirs with the shortest retention times also had the highest DA: RA ratios,*Cheatham, and *Cordell Hull (see Table 3):

- shortest retention times-- *Cheatham, *Cordell Hull, *Barkley, *Old Hickory
- largest local drainage areas--*Wolf Creek/Lake Cumberland, *Barkley, *Center Hill, *Cheatham
- largest lake size (water acres)--*Barkley, *Wolf Creek/Lake Cumberland, Dale Hollow,*Old Hickory
- highest DA:RA ratio--*Cheatham, *Cordell Hull, Martin's Fork, Center Hill

Historically, concentrations of nutrients in reservoir water inflows have been high, especially at J. Percy Priest, where the main water quality problem has been eutrophication from non-point sources (USACE, 1996). Suspended solids are generally lower on the main stem than the tributaries, due primarily to sedimentation behind the

dams. Besides non-point sources, the principal sources of contaminants in the CRB have historically been industrial effluents from the DuPont facility on Old Hickory reservoir, thermal discharges from TVA's Cumberland City and Gallatin, TN steam plants, and effluents from various municipal wastewater plants (USACE, 1996).

Land Use

Land use for the CRB reservoir watersheds was evaluated by use of the Multi-Resolution Land Characteristics Consortium's (MRLC) 2006 national land cover dataset (MRLC, 2011). The national land cover dataset products are created through a cooperative project involving multiple federal agencies. The 2006 land cover dataset is a 16-class land cover classification scheme applied consistently across the U.S. at a spatial resolution of 30 meters, based primarily on the unsupervised classification of Landsat Enhanced Thematic Mapper (ETM+) 2006 satellite data. The 2006 dataset for the CRB reservoir watersheds, along with the list of 16 cover classes, is given in Figure 2. The percent of each land cover type in each of the CRB reservoirs was estimated by clipping the raster and summing the counts for each land use type, by reservoir. Similar land cover types were combined for the following: developed land (use types 21-24); forests (41-43); scrub (51-52); "agriculture" (pasture/hay and cultivated crops, use types 81-82); and wetlands (land use types 90 and 95). The percentage of each land cover type, by reservoir, was plotted in Excel (Figure 2). As shown in Figure 2, the most developed lands were found in the watersheds for Cheatham (19 percent), Laurel (18 percent), and J. Percy Priest (16 percent). All watersheds were 40 percent or more forested. The highest

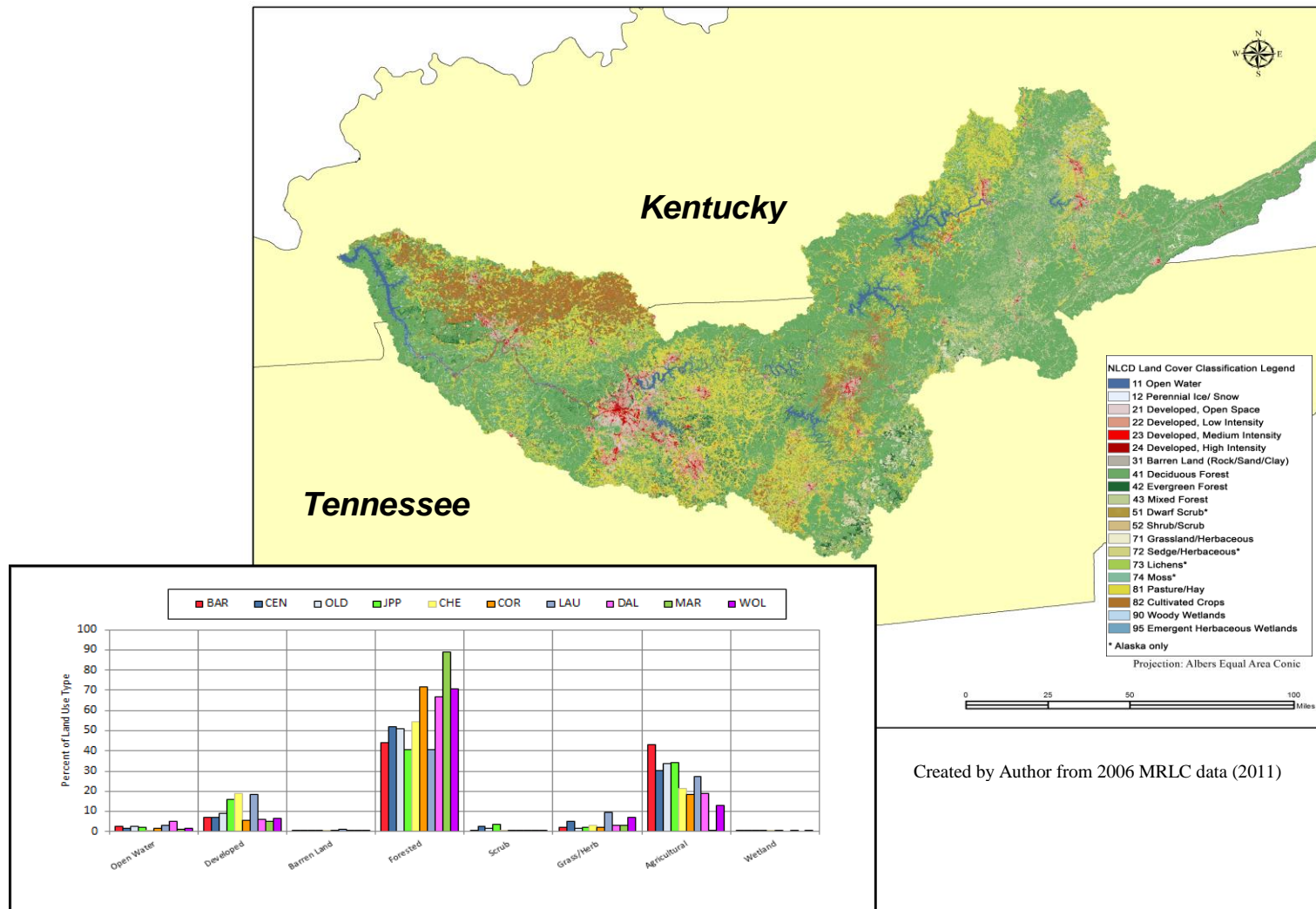


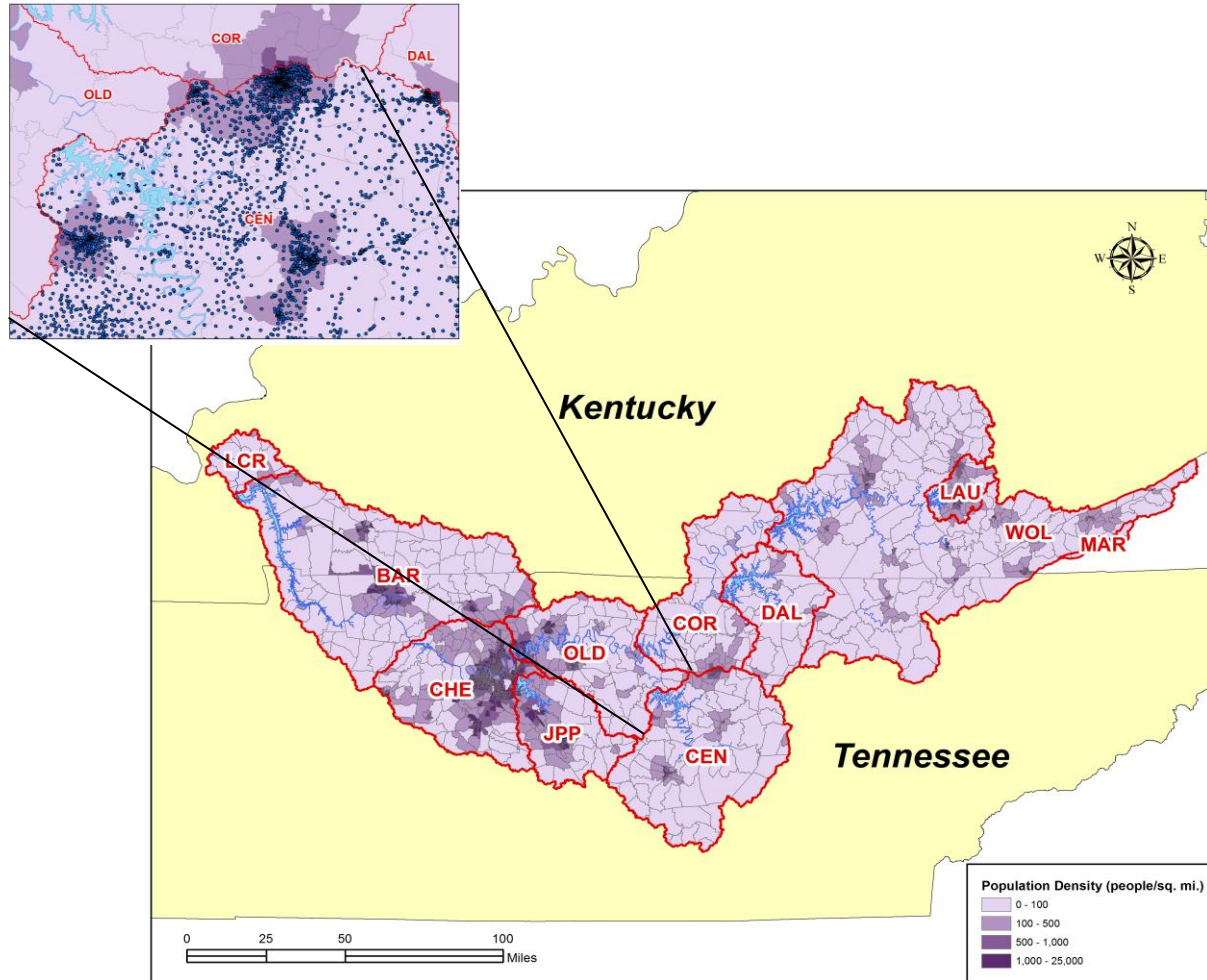
Figure 2. National Land Cover 2006 Dataset for the CRB

percentage of agricultural land was found for Lake Barkley (43 percent), and the lowest was found for Martin's Fork (1 percent), and Wolf Creek/Lake Cumberland (13 percent).

Population Density

U. S. Census population data in the form of the 2000 Census block centroids (ESRI, 2008) were used in GIS to estimate population density associated with each of the reservoirs. Population density was chosen as the measure of urban intensity for the CRB since it was the primary determinant in the 2009 USGS study, as well as a factor shown to be representative of urbanization in several other studies (USGS, 2009; Roy, et al., 2009; Chalmers, et al., 2007; Brown, et al., 2009). The 2000 Census was used because it was most representative of the time range from which sediment data were collected (1994-2010). Population density for each reservoir was estimated in GIS by clipping the block centroids with the CRB project boundaries, summing the area and population for each block within each reservoir, and then dividing the total population by the total land area, per reservoir. A portion of Center Hill reservoir is shown as an example (Figure 3). Although all but two reservoir areas (Dale Hollow, Martin's Fork) exceeded a total population of 50,000, none of the reservoir areas met the 2000 Census definition of "urban" based on population density (1,000 people per square mile). The highest population density was found for *Cheatham dam, at 380 people per square mile; this compares to the Nashville urbanized area of 1,730 people per square mile (see Figure 1).

Ranks were assigned to the most "urban" reservoirs based on population density (1 is highest). The most "urban" reservoirs were *Cheatham, J. Percy Priest, Laurel, and *Old Hickory. Of these, only *Cheatham and *Old Hickory are main stem reservoirs



Created by Author from 2000 Census data (2011)

Figure 3. 2000 Census Population Density of the CRB Watersheds

Priest; *Old Hickory, *Barkley, and *Cheatham (US Census, 2011). The three most “urban” reservoirs based on population density also correspond to the most “developed”, based on the 2006 MRLC dataset, i.e., Cheatham, J. Percy Priest, and Laurel.

Sediment Sampling and Laboratory Analysis

The sediment sampling program conducted by the Nashville District was initiated in 1994 under USACE guidance #1110-2-26, *Water Quality Investigations and Control Activities*, as part of the USACE’s water quality and water management mission (Tippit and Campbell, 2011). Every year, personnel from the Water Management Branch conduct water quality monitoring at all ten CRB reservoirs. Sampling covered a range of physical, chemical, and biological parameters (water data are not evaluated as part of this study); however, only the trace elements As, Be, Cd, Cr, Cu, Pb, Hg, Ni, and Zn are considered in this study. Each year, two reservoirs are also sampled for sediment contaminants on a rotating basis, so that every five years a complete round of reservoir sediment sampling is conducted. Therefore, every reservoir is monitored for sediment once every five years. The sediment sampling program is intended as a screening-level assessment of the general sediment quality throughout the CRB.

All sampling locations were biased; they were not randomly selected, but rather were collected in areas that are representative of conditions at the reservoir, and to illustrate a range of hydrologic conditions, such as the main channel, embayment, or forebay, etc. Samples were collected in the fall (September to November), and the same individual sampling locations within the reservoirs are sampled from year to year, generally within 500 feet. Only surficial (0 to 0.5 feet) sediment samples were collected; no cores or borings are part of this monitoring program. Consistency of sampling has been ensured because the same individuals have collected the samples over the years,

using the same equipment and same methods. Sediments were collected by boat, using a ponar dredge, and were homogenized by hand with a stainless steel spoon. Most sediments collected were in the silt and clay size range, but were not sieved (Tippit and Campbell, 2011). Sediments collected from Cheatham dam in particular tended to be more sand and gravel and less clay and silt than other reservoirs. Normalization of the data was not possible because the organic content and particle size of the sediments was not been determined, and aluminum has not been consistently measured throughout the monitoring period (Tippit and Campbell, 2011). The number of sediment sample locations and the depths of water from which the samples were collected varied, depending on the reservoir; generally, larger reservoirs had more samples (see Table 3).

Samples were analyzed by two different laboratories over the 1994-2010 time period. All trace elements except Hg were analyzed by method SW6010B, inductively coupled plasma/atomic absorption (ICP/AA), and Hg was measured by cold vapor (AA CVAA) (USEPA, 1994). Data were reported as totals, dry weight. Sediment chemistry data files were prepared by the USACE Nashville District Water Management Branch in Microsoft Excel and in GIS.

Data Analysis

It is well known that the interpretation of data from samples of environmental media collected for chemical analysis is complicated by the fact that all data are “left censored” because the lowest possible measured values are defined by the detection limit of the analysis. Thus, there are no zero results, and the lowest values, the below detection limit data, (or non-detects, NDs), are reported as “less than” a number (Helsel, 2010; Singh, 2006; Gilbert, 1987; USEPA, 1989, 2010). Results reported as NDs may actually range anywhere between zero and the detection limit. In addition, environmental data are

not often normally distributed, which precludes the use of classical (normal) statistics. Furthermore, samples collected over different periods of time, or collected by different labs, may have multiple detection limits. Performing the appropriate statistical analyses on such data is always a challenge, and has been the subject of debate for decades (Helsel, 1990, 2005, 2010; USEPA, 1989, 2010, 2011b).

There are two primary issues to resolve with environmental data: *what value to use to represent NDs*, and *what statistics to apply*? As reported by Helsel (2005), numerous environmental guidance documents have suggested methods for computing descriptive statistics for ND that are known to be flawed. The most commonly used methods to address ND data have been substitution methods where the ND data are typically replaced by zero, one-half (or another fraction) of the detection limit, or by the detection limit (Helsel, 2010). Substitution has been shown to result in variable results with high bias when calculating the mean, which worsens as the number of NDs increases (Helsel, 2005). Instead of substitution, other possible methods to handle NDs when computing descriptive statistics are parametric methods, including maximum likelihood estimation (MLE), imputation methods, such as regression on order statistics (ROS), or nonparametric methods, such as the Kaplan-Meier (KM) method, bootstrap techniques, the jackknife method, or the Winsorization method (Helsel, 2005; USEPA, 2010, 2011b). Singh, et al. (2006) concluded that the KM method is better than parametric methods under many circumstances. In the past, normal statistics were commonly used to estimate means and other summary statistics for environmental data without proving the distribution type; alternatively, it was often just assumed that all environmental data followed a lognormal distribution (USEPA, 1989; Helsel, 2005,

2010). Data distributions can be tested for goodness of fit, and nonparametric statistics can be used where the underlying data distribution is either unknown or unclear.

The USEPA also recommends use of the nonparametric Gehan test for hypothesis testing when data sets have multiple detection limits, as is the case with the Cumberland River Basin sediments (USEPA, 2011b; 2011c). The Gehan test is typically used to test whether a site concentration is different that background. The Gehan test was used here as a two sample, one-sided hypothesis test to estimate whether the mean concentration of a given trace element (the “site”) for one Cumberland Basin reservoir was greater than all others (the “background”). The Gehan test is a modification of the Wilcoxon Rank Sum test that tests for a location shift in the site concentrations (i.e., shift of the entire distribution). The Gehan test is a non-parametric test that utilizes only the rank of the concentrations, and thus it detects any upward shift of the concentration distribution of interest with respect to another group of data, such as background. The level of significance (α), chosen was 0.05. The p-value represents the probability that the null hypothesis (H_0), is true. The null hypothesis is rejected for all p-values less than the level of significance, and the alternative hypothesis is selected. The smaller the p-value, the stronger is the evidence for rejection of the null hypothesis. The p-values are computed using normal approximation for Gehan’s statistic, G, as follows (USEPA, 2011c):

$$G = \frac{\sum_{i=1}^N h_i a(R_i)}{\left[mn \sum_{i=1}^N \frac{[a(R_i)]^2}{N(N-1)} \right]^{\frac{1}{2}}}$$

where

m is background, and *n* is site measurements, ranked form smallest to largest, where the total number of combined samples is $N=m+n$,

R_i is the ranks for the N ordered data, and the N scores are $\alpha(R_i) = 2 R_i - N - 1$, where I is successively set equal to $1, 1, \dots, N$,

$h_i = 1$ if the i^{th} datum is from the site population
 $h_i = 0$ if the i^{th} datum is from the background population,

Form 1 (one-sided): If $G \geq z_{1-\alpha}$, then reject the null hypothesis that the site population median is less than or equal to the background population median (use z table for critical values).

ProUCL 4.1 is a free software package developed by the USEPA (USEPA, 2011b) to address the calculation of statistics for ND data; it was used to evaluate the USACE reservoir data for this study. In addition, GIS analyses were performed using ESRI ArcEditor 10.0 software. Nonparametric methods were used for all of the data analyses to be consistent, and to avoid having to prove data distributions. “Box and whisker” plots were also generated in ProUCL. Box plots show the data extremes (the “whiskers”) and medians, as well as the interquartile range (the width of the box), and are useful for showing how widely distributed the results are, and potential outliers in the data. ProUCL also plots the maximum non-detected value on the box plots. In addition, outliers were evaluated in ProUCL using both the Dixon test (n less than or equal to 25), and the Rosner test (n greater than 25); ND data were assumed to be equal to the detection limits for this analysis. Statistical outliers provide evidence that an extreme value does not fit the rest of the database. Outliers in a data set may be due to sampling and analysis errors, or may indicate the locations of hotspots (USEPA 2010).

CHAPTER FOUR: RESULTS AND DISCUSSION

Reservoir Concentration Comparisons

For each trace element, all data collected for all ten reservoirs were plotted on one graph. Box and whisker plots of the CRB sediment data generated in ProUCL are given in Figure 4 (As, Be, Cd), Figure 5 (Cr, Cu, Pb), and Figure 6 (Hg, Ni, Zn). Outlier tests conducted in ProUCL per the Rosner and Dixon tests, at a significance level of 0.10 or above, are indicated by a yellow circle around the data point in Figures 4, 5, and 6. The representative “baseline” trace element sediment concentrations from the USGS’s NAWQA sediment sampling, as reported by Horowitz and Stephens (2008), are also shown for comparison in each box plot as a horizontal red line. The entire sediment concentration data set is given in Appendix A.

As noted in Figures 4, 5, and 6, Ni was the only trace element detected in every single sample collected; Cr and Cu were also detected in all samples, with the exception of a few samples collected at Cheatham and J. Percy Priest. The median concentrations for all reservoirs were below the USGS’s baseline value for Be, Cr, and Cu. The median concentrations for Cd for all reservoirs exceeded the USGS’s baseline value, except for Center Hill and Old Hickory, and about half of the reservoir medians for Hg and Ni exceeded the USGS’s baseline values. The reservoir results are discussed individually below:

- **Lake Barkley.** No chemical concentrations were remarkable except Cd, which was highly variable; Cd also exceeded the USGS’s baseline value. Cu outliers were indicated for Barkley, but the USGS baseline value was not exceeded.
- **Center Hill.** The median value for As, Hg, Pb, and Zn exceeded the USGS baseline values. Cd outliers did not exceed the USGS’s baseline value. Outliers were observed for Cd, Hg and Zn.

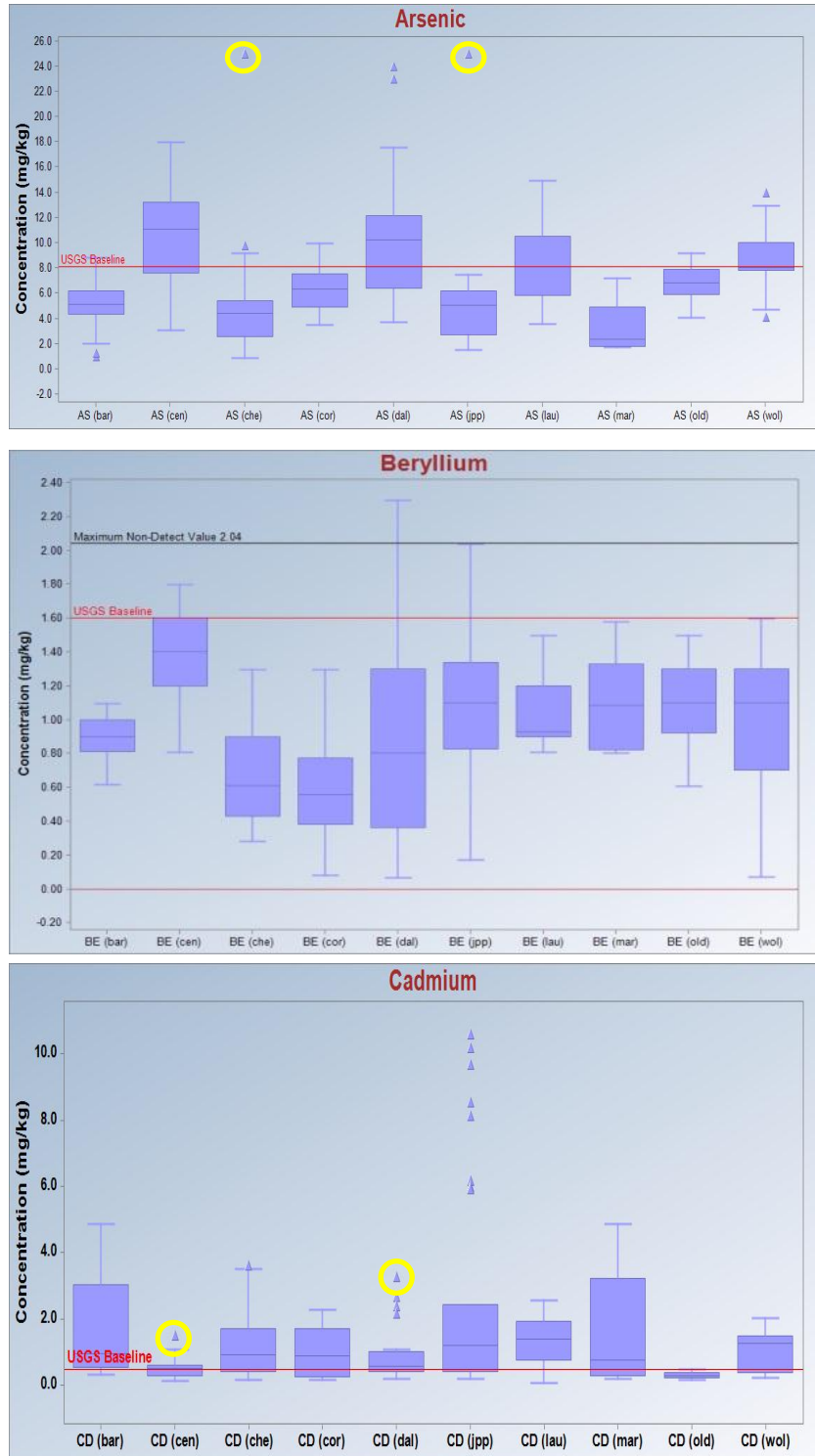


Figure 4. Range of Concentrations for CRB Sediment Samples, By Trace Element (As, Be, Cd) (1994-2010)

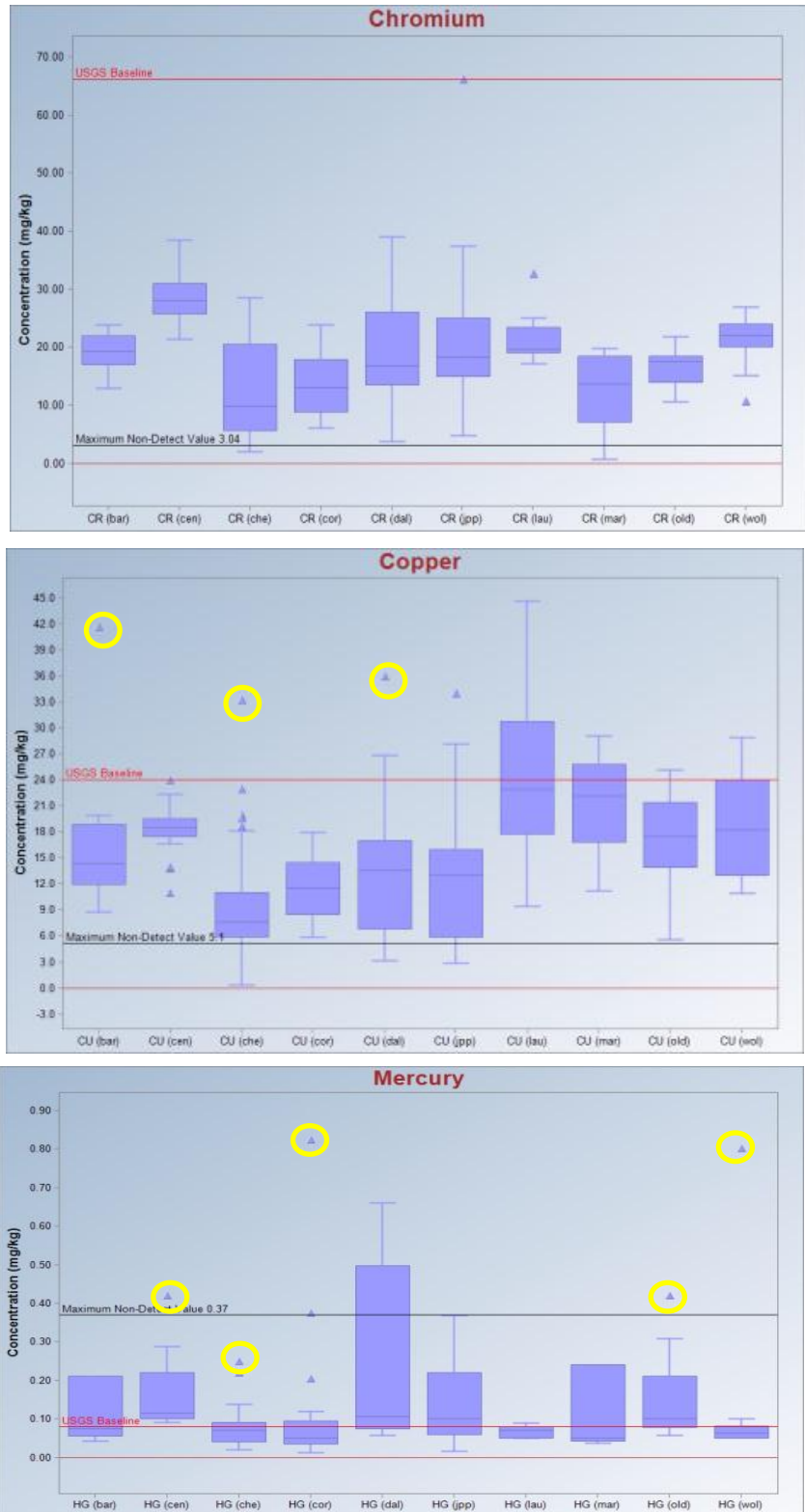


Figure 5. Range of Concentrations for CRB Sediment Samples, By Trace Element (Cr, Cu, Hg) (1994-2010)

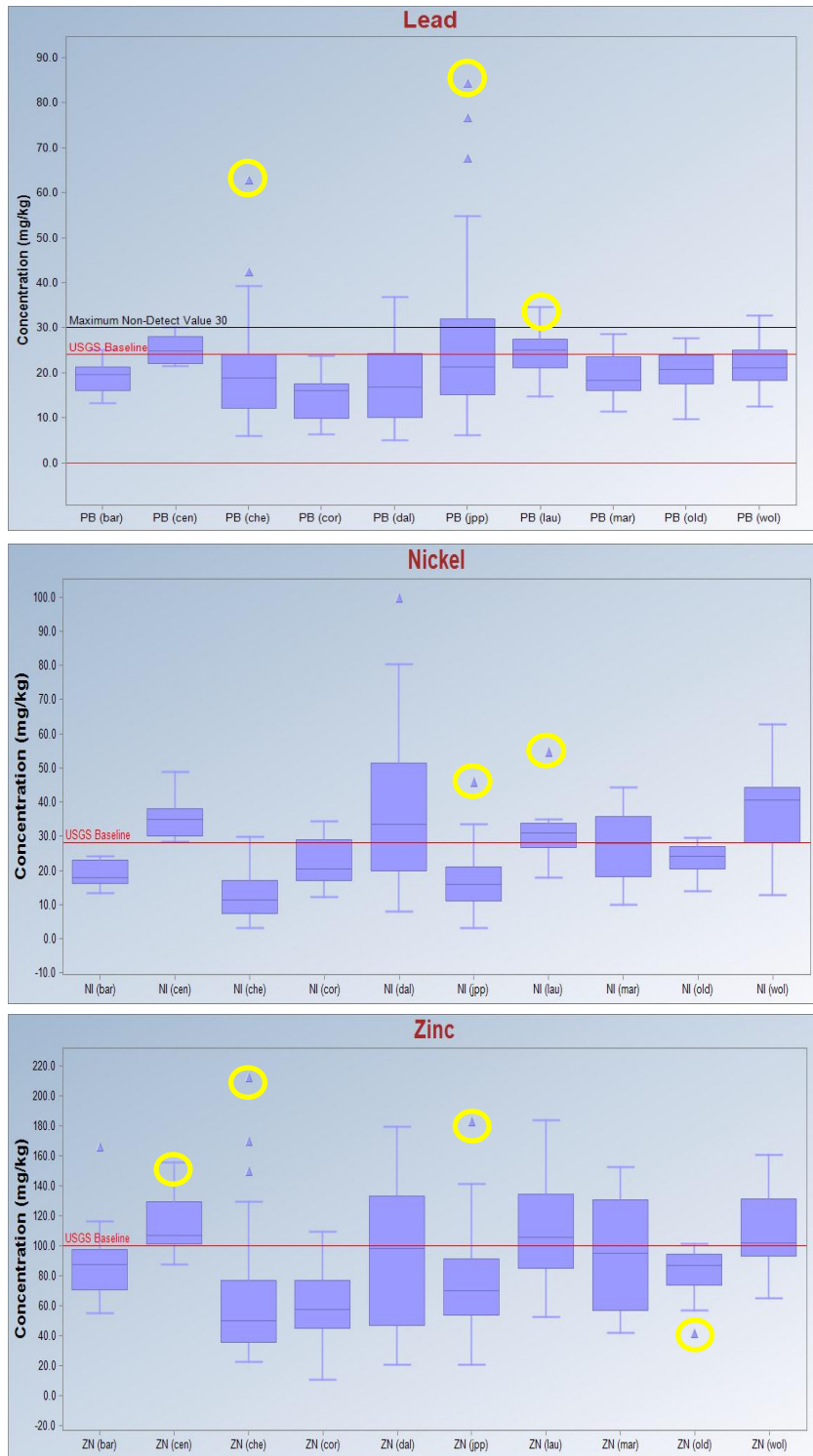


Figure 6. Range of Concentrations for CRB Sediment Samples, By Trace Element (Pb, Ni, Zn)(1994-2010)

- **Cordell Hull.** Cd exceeded the USGS's baseline value. Outliers were observed for Hg.
- **Dale Hollow.** Highly variable results were indicated for Be, Hg, Ni, and Zn. The median value for As, Cd, and Hg exceeded the USGS baseline value. Cd and Cu outliers were observed.
- **Laurel.** The USGS's baseline values for Cd, Pb, and Zn were exceeded. There were Ni and Pb outliers for Laurel.
- **Martin's Fork.** Cd and Zn results were highly variable; the Cd median also exceeded the USGS's baseline value.
- **Wolf Creek Dam/Lake Cumberland.** The median exceeded the USGS's baseline value for Cd and Zn. Outliers for Hg were observed.
- **Cheatham.** The Cd median exceeded the USGS's baseline value. As, Cu, Pb, and Zn outliers were indicated for Cheatham.
- **J. Percy Priest.** Outliers were observed for As, Pb, Ni, and Zn, but the USGS baseline values were not exceeded. The Cd and Hg USGS baseline values were exceeded.
- **Old Hickory.** Outliers for Hg were observed, and USGS baseline value was exceeded.

ProUCL was used to perform two sample, one-sided hypothesis testing using the Gehan test. Each reservoir was individually tested for each trace element against the concentrations for all other reservoirs (X) to determine if the individual reservoir was significantly different from X at the 0.05 confidence level. The null hypothesis was that the specific reservoir's trace element median concentration was less than or equal to X; the null was rejected if p was less than 0.05, i.e., the concentration of the reservoir was greater than all others. The p value is the smallest value for which the null hypothesis is rejected in favor of the alternatives; the greater the value, the higher the degree of trust in the null hypothesis (USEPA, 2010).

CRB reservoirs were ranked by the number of trace elements that were greater than all others, where 1 is high, or “worst” (Table 4). Center Hill ranked highest, as it had 8/9 trace elements (all but Cd) that were higher than all other reservoirs. The next highest ranking reservoirs were Wolf Creek/Lake Cumberland, Laurel, and Old Hickory. Of these, only Wolf Creek/Lake Cumberland is a main stem reservoir. Laurel and Old Hickory ranked in the top four most “urban” reservoirs (see Table 3). Copper was found to be significantly different more times than any other trace element (5 out of 10), followed by As, Cr, Hg, and Ni (each 3/10). Cheatham had the highest number of p values of “1”, indicating that there is no evidence to reject the null hypothesis. It may be also be concluded that most trace elements in Cheatham reservoir sediments are either lower or equal to those in all other reservoirs, as indicated in Figures 4, 5, and 6. It is interesting to note that of the three reservoirs found to be lower for all trace elements than all other reservoirs, Cordell Hull, Cheatham, J. Percy Priest, the latter two ranked as the two most “urban” reservoirs in the CRB (see Table 3).

Chalmers, et al. (2007) projected that, on average, trace elements concentrations double when a rural site becomes suburban, and triple when a suburban site becomes urban. Of the trace elements tested Cd, Cu, Pb, and Zn had the highest correlation to urbanization. Hollister, et al. (2008) evaluated the effect of scale and land use on estuarine sediments and found that Pb and Cu concentrations had the strongest relationship with developed land; Cd, Hg, and Zn showed a moderate association, and As and Cr were weakly associated. Furthermore, they found that Pb and Zn were significantly related to local (range of 15-20 kilometers) uses, suggesting that local sources were more important than distant land uses in the watershed for these trace

Table 4. Summary of Gehan Hypothesis Testing

p Values at 0.05 Confidence Level										Rank
Res.	As	Be	Cd	Cr	Cu	Pb	Hg	Ni	Zn	
*BAR	0.96	0.767	0.00192	0.237	0.279	0.667	0.73	0.95	0.69	5
CEN	3.10E-07	2.00E-06	0.957	1.90E-09	0.00295	1.60E-04	3.00E-06	1.80E-04	3.00E-06	1
*COR	0.419	1	0.474	0.996	0.993	1	0.906	0.555	0.995	6
DAL	1.9E-06	0.863	0.435	0.388	0.884	0.956	1.70E-04	5.70E-04	0.574	4
<i>LAU</i>	0.241	0.226	0.0478	0.0549	2.50E-04	0.00651	0.713	0.00718	0.137	3
MAR	0.999	0.0866	0.196	0.991	7.40E-04	0.617	0.984	0.117	0.0876	5
*WOL	0.0223	0.215	0.0686	0.00385	0.00427	0.14	0.541	9.30E-06	8.70E-06	2
* <i>CHE</i>	1	1	0.85	1	1	0.938	0.999	1	1	6
<i>JPP</i>	0.997	0.0832	0.0885	0.277	0.987	0.174	0.984	1	0.937	6
* <i>OLD</i>	0.168	0.0252	1	0.901	0.0159	0.398	0.00915	0.29	0.275	4

* Main stem reservoir. The most “urban” reservoirs, based on population density, are in italics (see Table 3).

Bold type means p was less than 0.05; reject the null hypothesis, reservoir concentration is greater than all others. Some reservoirs tied in rankings.

elements. Rice (1999) also found that trace elements characteristic of urban settings (Cu, sediment are similar to those in the literature for urban sediments; however, no other similarities were found for other trace elements. This may be due, in part, to high detection limits, especially at Cheatham.

Concentration Trends

Concentrations of each trace element are shown through time (1994-2010) in Figures 7, 8, and 9. Trends were evaluated by date and then by reservoir, with a moving average trend line; non-detect data were plotted at the detection limit. Selected highs and lows for reservoirs are shown in red and green letters, respectively. Sediment quality criteria levels called probable effects concentrations (PEC) values are also shown as dashed lines in Figures 7, 8, and 9 (there is no PEC for Be).

For most of the trace elements, there was not a clear pattern; concentrations tended to increase and decrease, without a large difference in minimum and maximum concentrations, such as for As, Cr, Ni, and Zn. The biggest range in concentrations appeared for Cd and Hg. A decreasing trend appeared for Pb after 1994; this is consistent with the findings of others who have observed decreased Pb concentrations in sediment since the ban of leaded gasoline (Callendar and Rice, 2000; Councell, et al. 2004). After a high in 1994, a decreasing trend appeared for Cd until about 2007, when concentrations generally increased. A similar trend was found and for Hg, which was highest in 1995, then decreased until 2006, when it generally started to increase. For a number of trace elements (Be, Cd, Cr, Cu, Ni, and Zn) there appeared to be a decrease between 2004 and 2005; 2004 was noted to be a “high water year” by the USACE (Tippit and Campbell, 2011). The reservoirs monitored during 2004 included Cheatham, and J. Percy Priest; reservoirs monitored in 2005 included Cordell Hull, and Dale Hollow.

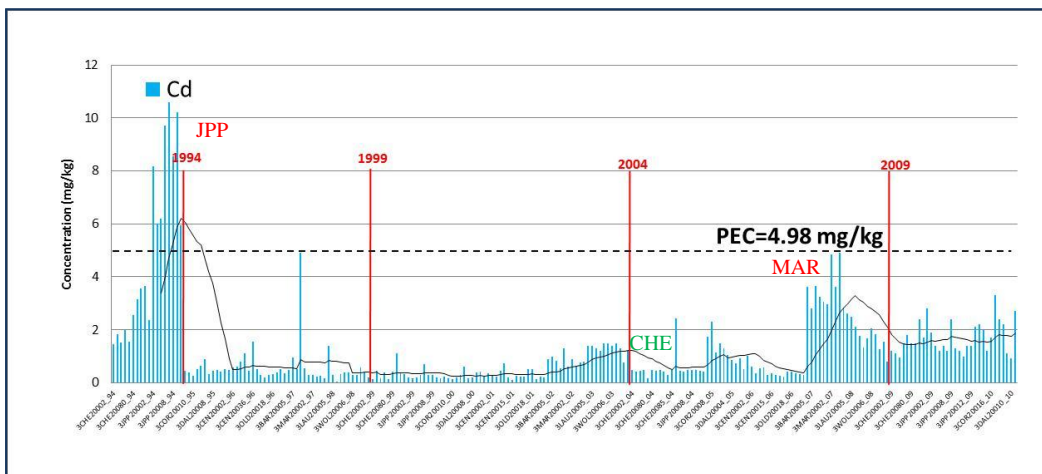
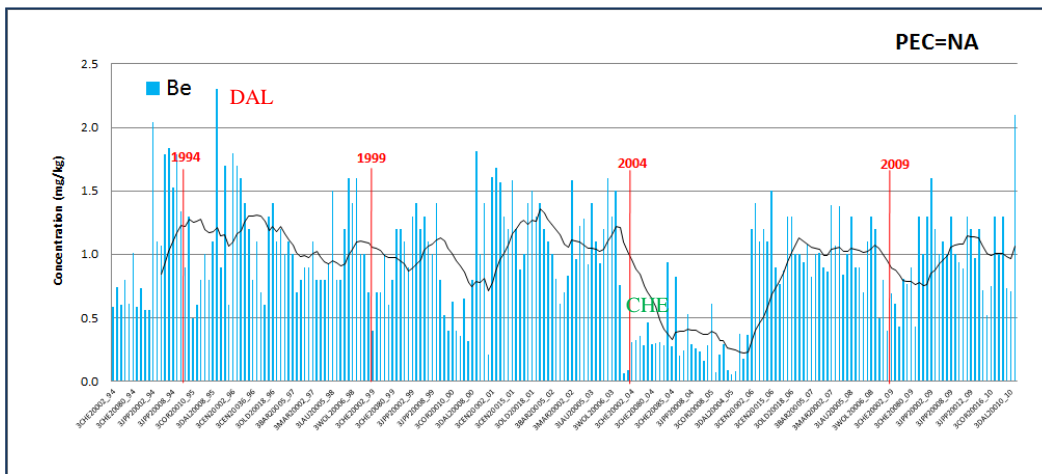
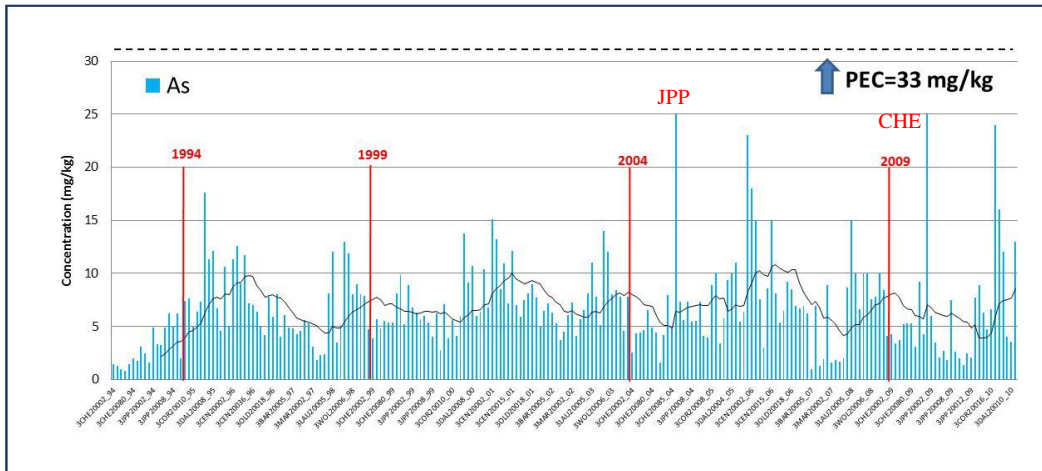


Figure 7. Concentrations of CRB Sediments (As, Be, Cd), By Year (1994-2010)

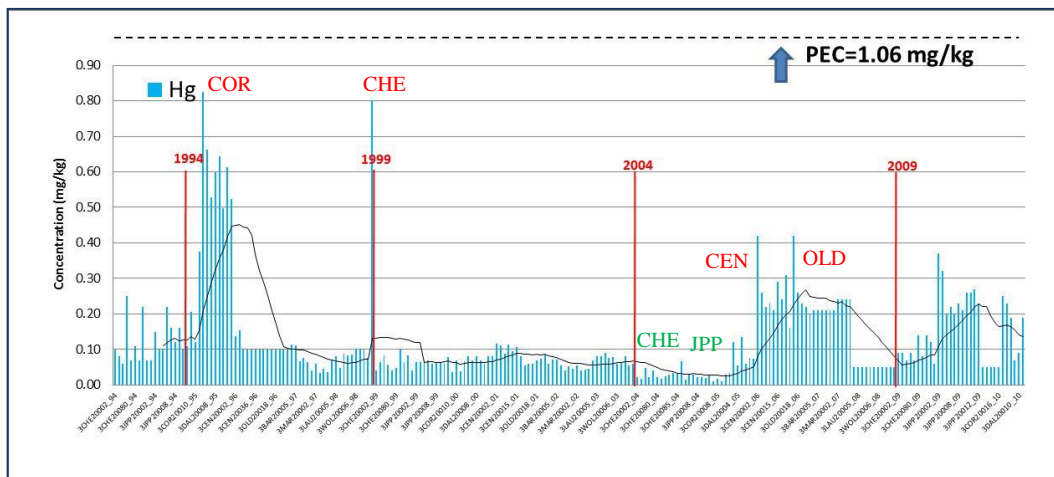
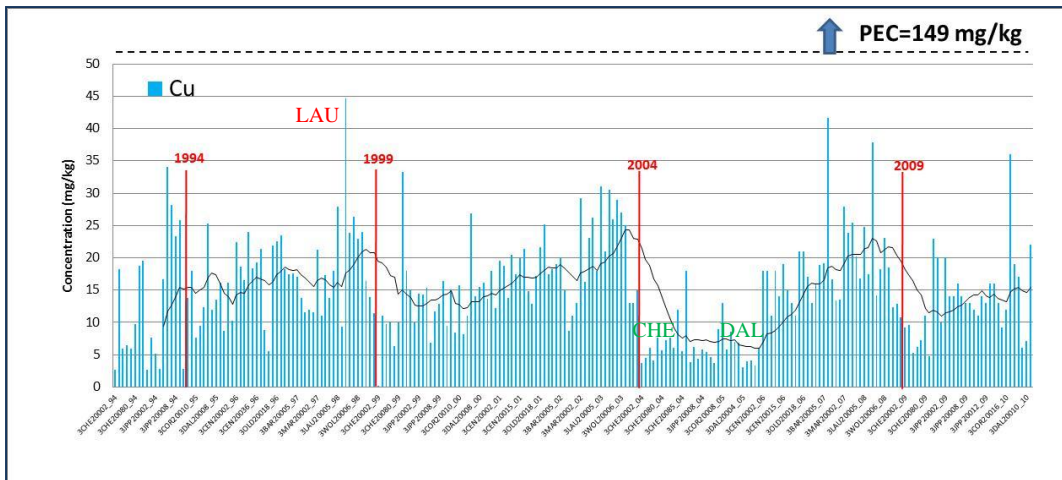
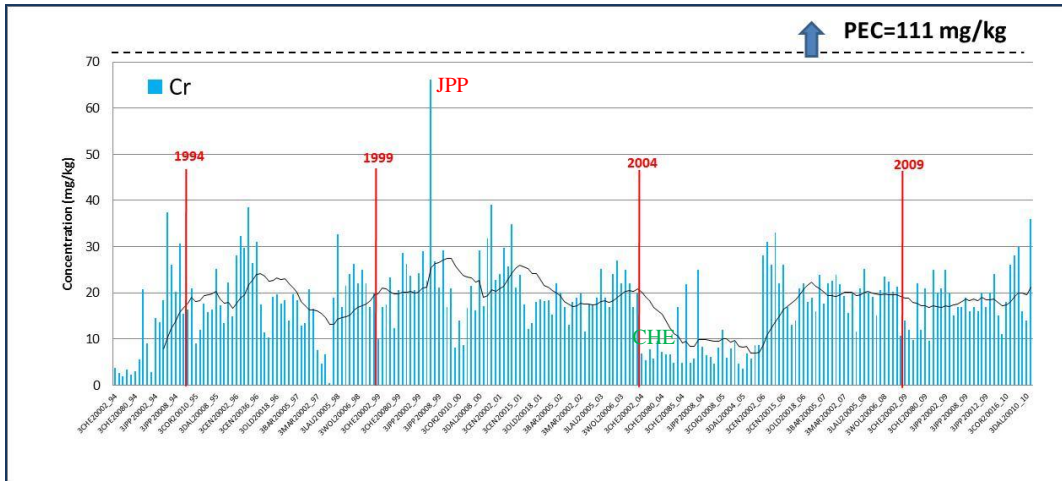


Figure 8. Concentrations of CRB Sediments (Cr, Cu, Hg), By Year (1994-2010)

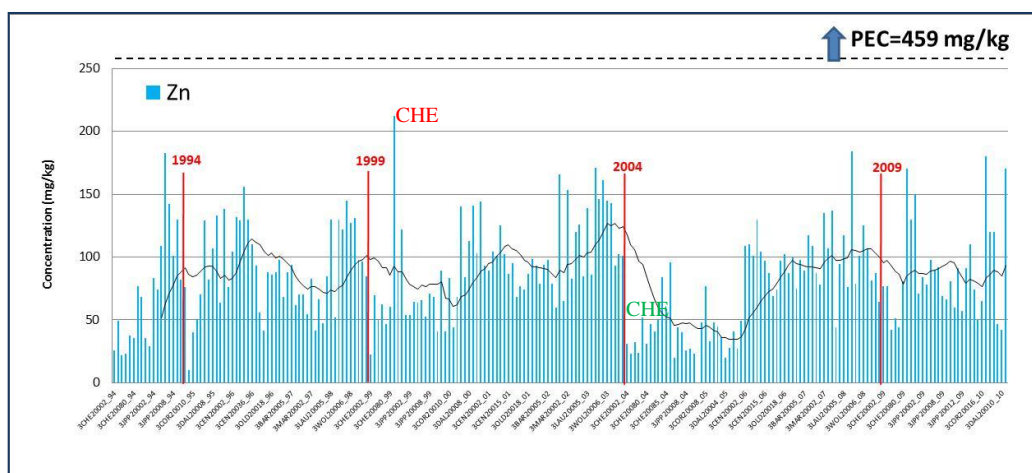
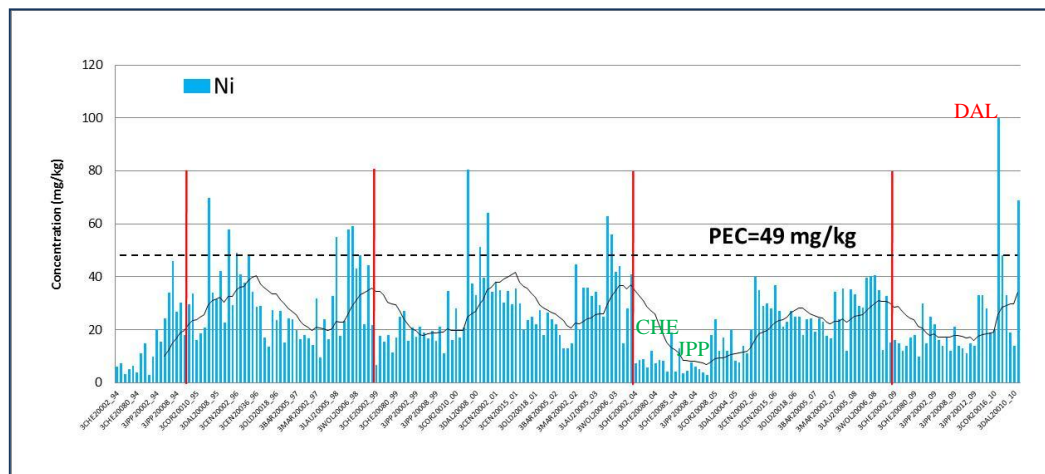
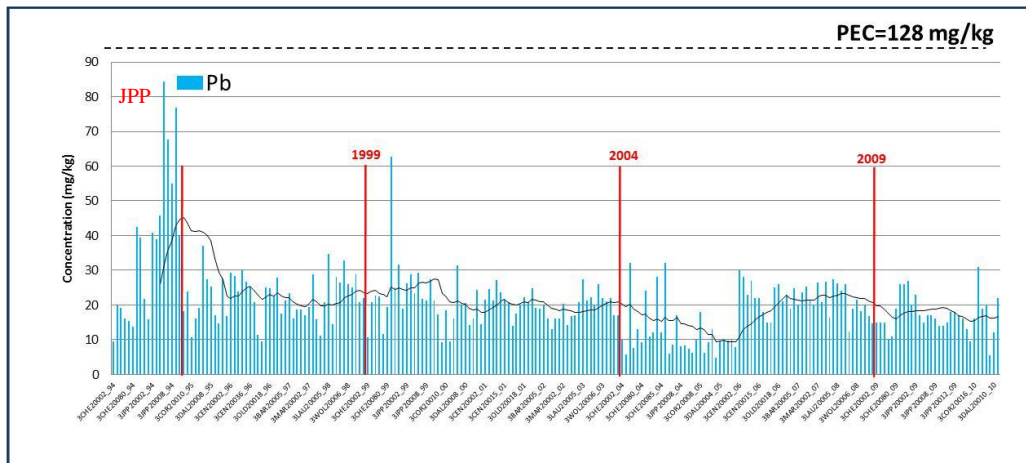


Figure 9. Concentrations of CRB Sediments (Pb, Ni, Zn), By Year (1994-2010)

An evaluation of concentration trends through time for the CRB is a little misleading because not all lakes were analyzed for all years (each reservoir was measured once every five years). Therefore, some peaks may be due to circumstances at certain reservoirs, rather than a trend in the trace element concentrations. Similar plots of concentrations were also prepared by sample depth and by sample location (embayment, main channel, forebay), but no trends were obvious, and they are not presented here. In addition, with the sampling design used, it was not possible to distinguish possible surface water contaminants from potential atmospheric sources for the CRB sediments.

The CRB findings are not as conclusive as other trace element sediment trends noted in the literature. As part of the NAWQA program, Mahler, et al. (2006) evaluated national historical trends in trace element concentrations in sediment cores from 35 lakes and reservoirs collected from 1996 to 2001 from primarily urban locations (none were located in Kentucky or Tennessee). They found that decreasing trends outnumbered increasing trends for all seven elements evaluated (Cd, Cr, Cu, Pb, Hg, Ni, and Zn). The most pronounced changes were observed by Mahler, et al. for Pb (83 percent of the lakes had decreasing trends, and 6 percent had increasing trends) and Cr (54 percent had decreasing trends, and none had increasing trends). Collectively, the change in means for all metals was -7 percent, ranging from Pb at -28 percent to Zn at +2 percent. Zinc was found to be increasing, especially in dense urban watersheds. Mahler, et al. (2006) concluded that the source of Hg and Ni was likely atmospheric, but the transport pathway to urban lakes was fluvial; conversely, urban inputs via water for Pb and Zn generally overshadowed regional atmospheric sources. Chalmers, et al. (2007) found similar

declining trends for metals (Cd, Cr, Cu, Ni, Pb, Hg, Zn) in lake sediments in New England from 1965 to 2000.

In a number of instances in the CRB sediments, there were very high non-detect levels (compared to SW846 method detection limits) for several trace elements, including numerous non-detect limits in the 60 to 170 mg/kg range for Zn; the SW846 method detection limit is 2 mg/kg (USEPA, 1994). In addition to high detection limits, there were some reservoirs that had more ND data than others, and some trace elements that were not detected more often than others. By far, Cheatham had most ND data: As (8/41); Be, (10/41); Cd (15/41); Hg (16/41); and Zn (11/41). Other reservoirs had high numbers of non-detect data, but for fewer elements: J. Percy Priest (Hg 17/35); Dale Hollow (Zn 7/26); Wolf Creek/Lake Cumberland (As 7/21); and Old Hickory (Cd 9/24). Mercury (Hg) had the highest percentage of non-detects compared to other trace element (34 percent for all reservoirs combined), and was often found to have detection limits higher than the method detection limit of 0.1 mg/kg. Nickel was the only trace element detected in every single sample collected, and Cr and Cu were also detected in all samples, with the exception of a few samples collected at Cheatham and J. Percy Priest, respectively. The USACE has observed that the Cheatham sediment samples often had a high water content (Tippit and Campbell, 2011), which may result in higher detection limits if there was insufficient sample volume for analysis. Furthermore, since the CRB Basin sediment samples are not sieved, the high number of ND values and the high levels of ND detection limits may be the result of analyzing coarser grained sediment fractions that would not be expected to adsorb trace elements. Since coarser particles tend to have

lower concentrations of metals, a high proportion of coarse particles in a sample tends to dilute the whole sample; this is known as “the matrix effect” (Ongley, 1996).

Comparison to Probable Effect Concentrations

To evaluate the potential environmental relevance of the trace element concentrations in the CRB reservoir sediments, the concentrations were compared to the sediment PECs. PECs are a consensus of six different sets of published sediment quality guidelines based on toxicity to a variety of benthic organisms. Concentration of a trace element in sediments above the corresponding PEC is expected to cause adverse effects to benthic biota in freshwater ecosystems. PEC quotients (PECQs) are often calculated to show the relative toxicity of a contaminant. The PECQ is the mean of the trace element concentration divided by the PEC value; a PECQ greater than 1 is a good indicator of toxicity (MacDonald, et al., 2000). None of the trace elements had an individual PECQ of 1.0 or more. The only PECQs that exceeded 0.5 were Cd (for J. Percy Priest only), and Ni (for Center Hill, Dale Hollow, Laurel, Martin’s Fork, and Wolf Creek/Lake Cumberland).

As a measure of overall sediment quality between reservoirs, a metals contaminant index (MCI) (Mahler, et al., 2006) was calculated by summing the PECQs and dividing by the number of contaminants; the MCI values were then ranked (1 is the highest toxicity). The highest ranking (“worst”) MCI values were for Center Hill, Dale Hollow, Wolf Creek/Lake Cumberland, and Laurel. The lowest ranking (“best”) MCI values were for Cheatham, Cordell Hull, Old Hickory, and Barkley (Table 5).

Potential Sources

The USEPA’s geospatial database (USEPA 2011d) was used to evaluate potential primarily industrial and municipal point sources of contaminants to the two “worst” CRB

Table 5. Summary of Metal Contaminant Index Calculation and Rank

Reservoir	PEC Quotient (Mean Detected Concentration/PEC)									Metals Contaminant Index (PECQ/n x 1000)	Rank
	As	Be	Cd	Cr	Cu	Pb	Hg	Ni	Zn		
*BAR	0.15	NA	0.36	0.17	0.11	0.15	0.11	0.39	0.19	203	7
CEN	0.32	NA	0.11	0.26	0.12	0.20	0.15	0.73	0.24	267	1
*COR	0.19	NA	0.21	0.12	0.08	0.11	0.11	0.46	0.13	176	9
DAL	0.31	NA	0.18	0.17	0.09	0.14	0.22	0.78	0.20	263	2
LAU	0.26	NA	0.27	0.19	0.17	0.19	0.06	0.64	0.24	253	4
MAR	0.10	NA	0.34	0.11	0.14	0.15	0.10	0.55	0.21	214	6
*WOL	0.26	NA	0.21	0.19	0.13	0.17	0.10	0.78	0.24	260	3
*CHE	0.15	NA	0.24	0.11	0.07	0.15	0.07	0.25	0.14	147	10
JPP	0.16	NA	0.51	0.18	0.09	0.21	0.12	0.33	0.16	220	5
*OLD	0.20	NA	0.07	0.15	0.12	0.16	0.13	0.48	0.18	185	8
PEC	33	NA	4.98	111	149	128	1.06	49	459	—	—

* Main stem reservoir.

NA= PEC not available for Be.

Mean detected concentrations were total, dry weight (mg/kg).

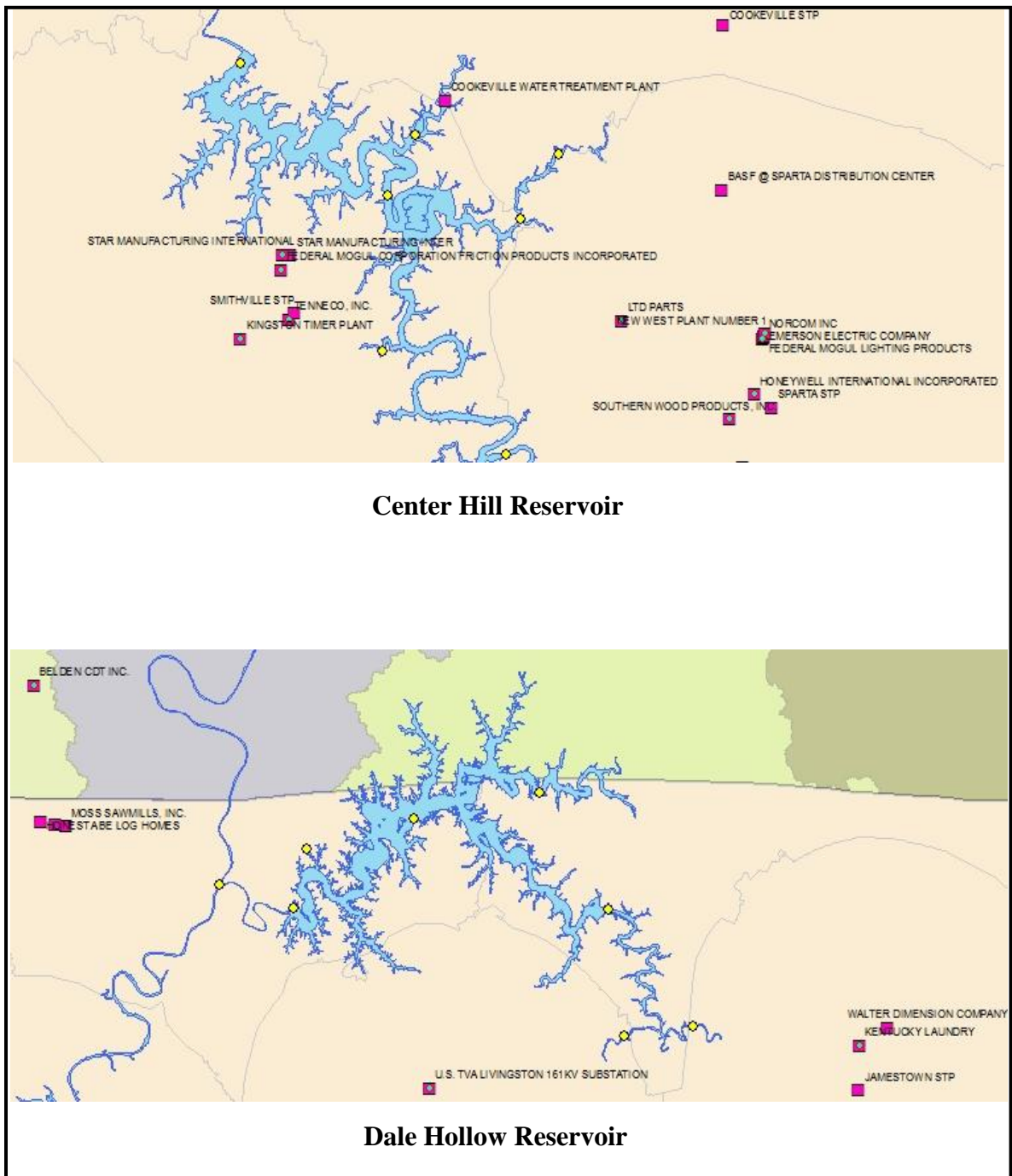
PEC = probable effects concentration for aquatic toxicity; PEC Quotient (PECQ) = mean concentration/PEC ; PECQ of 1 or greater is an indicator of toxicity.

Metals Contaminant Index (MCI) = PECQ/ number of contaminants.

reservoirs, based on the MCI rank: Center Hill and Dale Hollow. The database is very comprehensive and updated often; it contains spatial representations and limited facility data from the following databases maintained by the USEPA: the CERCLA (Superfund) National Priorities List of abandoned hazardous waste sites; RCRAInfo, the list of active hazardous waste large quantity generators and treatment, storage, disposal facilities; the Integrated Compliance Information System (ICIS), the Permit Compliance System (PCS); the NPDES list of permitted water dischargers; the Air Facility System (AFS), the list of major dischargers of air pollutants; the annual Toxic Release Inventory (TRI) system; the Section Seven Tracking System (SSTS) for pesticides; and ACRES, which lists Brownfields Properties.

For Dale Hollow, there are very few industrial and municipal sources near the reservoir, and none which would appear to contribute significant levels of trace elements to reservoir sediments. Although there are more potential sources located near Center Hill than Dale Hollow, the data available for the facilities do not indicate that any would be potential sources of trace elements (Figure 10) (USEPA, 2011d).

The most recent 303(d) lists for both Kentucky and Tennessee were consulted to determine if any of the CRB reservoirs were considered to be impaired. For Kentucky, the latest 303(d) list was the final list from 2008. The only CRB reservoirs that were mentioned were Lake Cumberland/Wolf Creek for methylmercury from atmospheric deposition, and Laurel reservoir for a variety of causes, including: mining, temperature, sedimentation/siltation, fecal coliform, sulfates, organic, conductance, and phosphorus (KDEP, 2008). The source of the mercury was not noted in the report. For Tennessee, the only CRB reservoirs noted as impaired were portions of Lake Barkley for thermal



Source: Created by Author (2011) using USEPA's Geospatial database (April, 2011).

Figure 10. Potential Point Sources From USEPA's Geospatial Database

impairment from the Cumberland Steam Plant, and portions of Cheatham, for bacteria (TDEC, 2010).

Study Limitations

Although the CRB sediment sampling program has been long-term and consistently executed, there are some limitations in the data that should be considered when evaluating the results. First, it is intended as a screening program, so it does not require the rigor of a different sampling regime, such as for permit compliance. Also, the frequency and spatial extent of sampling data vary by watershed; not all of the reservoirs are sampled every year which makes a true annual comparison not possible. The biggest difference in the CRB program compared to many of the studies in the literature is that the sediments are not sieved so that just the silt/clay fraction is accounted for, where most trace element concentrations would be expected to be found. Also, as noted previously, some of the lab results had very high detection limits, making it appear that a contaminant was not detected when it really might have been, if a lower detection limit was achieved; this may be because of the lack of sieving of the sediments. Although a bigger watershed may be expected to have the potential for more contamination, the size of the drainage area does not address the possible intensity of land use or population density. There are also problems of scale. Localized problems and sources in specific reaches might be expected to reflect intensity of land use in the vicinity, but may not be useful in interpreting larger trends in the entire watershed. Potential contaminants like trace elements that are long-lived and not readily degraded in the environment have been cycled in sediments for many years, and may have been transported far from their original source.

CHAPTER FIVE: CONCLUSION

The sediment sampling program conducted by the USACE on the CRB over the last 17 years indicated trace element levels that were generally consistent with national baseline (“background”) concentrations measured by the USGS in the NAWQA program. Individual locations exceeded the USGS values for some trace elements, with Cd, Hg, and Ni the elements exceeding the USGS levels most often. Copper did not exceed the USGS levels in any sediment samples collected in the CRB. Nickel was the only trace element detected in every sediment sample collected. No remarkable trends through time were observed for the CRB sediments, although it appears that Pb levels have decreased over the years that the sediments have been collected, and that Cd and Hg levels have been rising since about 2006. However, Hg had 34 percent non-detect values for sediments collected from all reservoirs, and many of the sample detection limits were higher than the method detection limit for Hg. The USACE should consider reevaluating its current analytical methods and reporting limits, in addition to sieving sediments in the future to facilitate comparison of concentrations between reservoirs.

In comparing the sediment concentrations from one reservoir to another, Center Hill had the greatest number of trace element concentrations (8/9, all except Cd) that were statistically significantly greater than all other reservoirs. Although Cu in CRB sediments did not exceed the USGS baseline levels, Cu was significantly higher more times than any other trace element (5 out of 10), when comparing concentrations among reservoirs.

The results of this study showed that although land use was correlated to population density in the CRB watersheds, population density was not necessarily

correlated with sediment quality. Watersheds with higher portions of developed land usually are more urbanized, and that trend was also found in the CRB. Use of the 2006 MRLC dataset to estimate the percentage of land cover type in each CRB reservoir watershed showed that Cheatham, J. Percy Priest, and Laurel were found to have the most “developed” land. Population density estimates from the 2000 Census used as a measure of urbanization in the Cumberland River reservoir watersheds showed that these three reservoirs also ranked as the “most urban”. The urban rankings based on the 2000 Census data, therefore, are consistent with the estimates of developed land based on the 2006 MRLC dataset.

Based on the literature reviewed, it was expected that the most urban CRB reservoirs would have the highest (“worst”) concentrations of trace elements in the sediments sampled. Three out of the top four “worst” reservoirs based on aquatic toxicity (Center Hill, Wolf Creek/Lake Cumberland, and Laurel), were also in the top four reservoirs with the highest concentrations that were significantly different than all others, based on the Gehan test. However, applying aquatic toxicity value comparisons as a measure of sediment quality, there was no obvious correspondence between the degree of urbanization of the CRB reservoir drainage areas and sediment quality. In addition, there did not appear to be any correspondence with sediment quality and the drainage area/reservoir area ratios of the CRB reservoirs.

Surprisingly, reservoirs with the “worst” sediment quality (Center Hill, Dale Hollow, Wolf Creek/Lake Cumberland, and Laurel), in terms of aquatic toxicity comparisons, were not the most urban, but the reservoirs with the *longest retention times*. Furthermore, the reservoirs with “best” quality, in terms of aquatic toxicity comparisons,

were the most urban reservoirs, Cheatham and Old Hickory, followed Cordell Hull and Barkley; these four reservoirs also have the four shortest retention times. Therefore, it may be concluded that retention time may have a more significant effect on CRB sediment quality than urbanization. This is a logical finding, as sediment concentrations do not have time to accumulate in reservoirs with short retention times.

Historically and currently, the majority of the non-point source “best management practices” for surface water are based on the well-accepted assumption that land use activities directly impact water and sediment quality (USEPA, 2005). The findings of this study, however, is not completely consistent with other’s findings that showed a correlation between population density and sediment concentration (USGS, 2009; Roy, et al., 2009; Chalmers, et al., 2007; Brown, et al., 2009).. There are several possible explanations for this difference. First, none of these studies in the literature reported the hydrologic characteristics of the water bodies they evaluated in terms of retention time. Also, none of these studies evaluated sediment quality based on aquatic toxicity; quality was based solely on concentration. Furthermore, although not evaluated in this study, it is possible that some of the contamination of CRB reservoir sediments comes from atmospheric deposition, rather than being directly associated with “developed” land uses, or the degree of urbanization of the watershed. Sources of atmospheric deposition are present in rural areas (e.g., power plants), and atmospheric contaminants have been shown to travel great distances from their sources. The USEPA has found that atmospheric sources were the greatest sources of water quality impairment in lakes and reservoirs; thus, these types of sources may warrant more evaluation in terms of non-point source pollution, especially for Hg.

The results of this study indicate that it may be prudent to include an evaluation of quality based on aquatic toxicity when sediment monitoring sediment quality, and that when reservoirs are the subject of sediment quality assessments, the consideration of the physical properties of the reservoir, especially the retention time, is essential for a comprehensive evaluation. This may also imply that sediment quality in reservoirs may be effectively regulated by water resource management techniques at the reservoirs that affect retention time.

APPENDIX A SUMMARY OF CRB SEDIMENT DATA

Reservoir	Station	Sample Year	Sample Depth (feet)	Sediment Concentration, dry weight (mg/kg)								
				As	Be	Cd	Cr	Cu	Pb	Hg	Ni	Zn
BAR	3BAR20002	1997	64	4.9	1.1	0.48	19.7	17.6	21.2	0.113	24	88.2
BAR	3BAR20002	2002	66	7.2	1.1	0.88	22	19	19	0.072	24	< 94
BAR	3BAR20002	2007	63	6.2	1.1	3.63	23.9	18.9	24.8	< 0.210	24.2	97.5
BAR	3BAR20005	1997	50	4.8	1	0.95	18.4	17.1	23.3	0.112	19.8	93.9
BAR	3BAR20005	2002	46	6.3	1.0	0.97	20	20	20	0.071	22	< 98
BAR	3BAR20005	2007	49	1	0.82	2.82	17.6	19.1	20	< 0.210	19.3	88.9
BAR	3BAR20006	1997	35	4.3	0.7	0.52	12.8	13.8	16.1	0.067	16.3	61.7
BAR	3BAR20006	2002	32	5.3	0.81	0.83	17	15	16	0.055	18	< 79
BAR	3BAR20006	2007	43	6.9	1	3.65	22	41.7	23.7	< 0.210	24.4	117
BAR	3BAR20007	1997	17	4.6	0.8	4.9	13.4	11.6	18.6	0.076	18	70.3
BAR	3BAR20007	2002	14	3.7	0.61	0.56	13	8.7	13	0.041	13	< 60
BAR	3BAR20007	2007	26	1.3	1.01	3.24	22.6	16.6	25.2	< 0.210	23.1	109
BAR	3BAR20031	1997	23	5.6	0.90	0.53	20.7	11.9	18.8	0.064	16.6	70.5
BAR	3BAR20031	2002	12	4.5	0.70	1.30	18	11	16	0.052	13	< 166
BAR	3BAR20031	2007	24	1.9	0.90	3.05	23.8	13.4	21.2	< 0.210	17.7	87.2
BAR	3BAR20032	1997	16	5.3	0.90	0.31	16.6	11.5	17	< 0.040	14.4	54.2
BAR	3BAR20032	2002	16	6.1	0.83	0.61	19.0	13	16	0.045	15	< 65
BAR	3BAR20032	2007	20	8.9	0.86	2.95	21.9	13.5	20	< 0.210	16.8	77.9
CEN	3CEN20002	1996	150	11.3	1.80	0.582	28.0	22.4	29.3	0.137	49	104
CEN	3CEN20002	2001	161	15.1	1.61	0.26	24.1	19.5	21.5	0.117	37.7	89
CEN	3CEN20002	2006	157	18.0	1.20	< 0.61	28	18.0	< 30	0.420	40	109
CEN	3CEN20004	1996	120	12.6	1.70	0.597	32.3	18.6	28.4	0.155	41	132
CEN	3CEN20004	2001	130	13.2	1.68	0.23	29.7	18.7	24.5	0.111	34.9	104
CEN	3CEN20004	2006	131	15.0	1.40	0.35	31	18	28	0.260	35	110
CEN	3CEN20007	1996	68	9.0	1.60	0.79	29.7	16.5	23.8	< 0.100	37.9	129
CEN	3CEN20007	2001	70	8.5	1.57	0.44	25.7	13.8	21.3	0.089	30.3	101
CEN	3CEN20007	2006	70	7.6	1.10	0.56	26.0	11	23	0.220	29	101
CEN	3CEN20008	1996	55	11.7	1.40	1.10	38.6	24	30.3	< 0.100	48	156
CEN	3CEN20008	2001	63	10.9	1.30	0.74	34.8	20.5	27.1	0.113	34.7	125
CEN	3CEN20008	2006	65	3	1.2	0.59	33.0	18	27	0.230	30	130
CEN	3CEN20010	1996	50	7.1	1.2	0.44	26.5	18.4	26.8	< 0.100	34.2	130
CEN	3CEN20010	2001	57	7.2	1.2	0.20	21.2	17.5	23.7	0.096	29.5	102.0
CEN	3CEN20010	2006	60	8.6	1.1	0.28	22.0	14.0	22.0	0.210	28.0	104.0
CEN	3CEN20015	2001	108	12.1	1.58	0.12	23.8	19.9	21.5	0.107	35.6	86.7
CEN	3CEN20015	2006	107	15.0	1.5	0.37	26.0	19.0	22.0	0.290	37.0	97.0
CEN	3CEN20036	1996	5	7.0	0.8	1.54	31.0	19.3	25.2	< 0.100	28.6	110.0
COR	3COR20002	1995	62	7.42	0.9	0.449	16.3	13.8	18.1	0.11	29.7	76.4
COR	3COR20002	2000	62	7.1	0.52	0.22	20.9	15.1	17.2	0.078	34.5	88.9
COR	3COR20002	2005	62	3.98	0.280	1.75	8.2	8.94	10	0.011	18	48.0
COR	3COR20002	2010	70	7.7	0.970	2.1	20.0	16	17	< 0.050	33	91.0
COR	3COR20008	1995	36	7.65	1.3	0.397	20.9	18	23.9	0.205	33.8	10.3
COR	3COR20008	2000	35	3.90	< 0.4	0.17	8.0	8.37	9.3	0.036	16	41.0
COR	3COR20008	2005	36	8.86	0.614	2.31	12.0	13	18	0.018	24	77.0
COR	3COR20008	2010	37	8.90	1.200	2.20	24.0	16	16	< 0.050	33	110.0
COR	3COR20010	1995	14	5.04	0.5	0.275	9.0	7.6	10.6	0.12	16.1	40.2
COR	3COR20010	2000	10	5.60	0.63	0.13	14.0	15.8	18.5	0.068	28	83.0
COR	3COR20010	2005	8	< 10	0.073	1.15	5.9	5.76	6.13	< 0.010	12	33.0
COR	3COR20010	2010	6	6.3	0.720	2.00	15.0	13.00	13.00	< 0.050	28	74.0
COR	3COR20013	1995	10	6.4	0.6	0.51	11.9	9.5	16.1	< 0.375	18.6	50.3
COR	3COR20013	2000	30	4.1	< 0.4	0.19	8.7	8.1	9.5	0.038	17.2	44.3
COR	3COR20013	2005	10	3.37	0.207	< 1.48	7.9	8.54	9.37	0.030	17	48.0
COR	3COR20013	2010	28	4.70	0.520	1.20	11.0	9.20	9.50	< 0.050	19	50.0
COR	3COR20016	1995	18	7.3	0.8	0.64	17.7	12.4	19.2	0.825	20.9	70.5
COR	3COR20016	2000	18	5.9	0.36	0.28	16.8	11.1	16	0.066	20.7	68.1
COR	3COR20016	2005	20	5.77	0.290	1.31	9.4	7.01	13	0.034	12	45.0
COR	3COR20016	2010	20	6.60	0.750	1.70	18.0	12	16	< 0.050	20	65.0
DAL	3DAL20002	1995	135	17.6	1.00	0.88	15.9	25.3	37.0	0.663	69.8	129.0
DAL	3DAL20002	2000	130	13.8	0.65	0.62	21.5	26.9	31.3	0.080	80.5	140.0
DAL	3DAL20002	2005	134	9.34	0.085	1.04	4.6	6.80	4.80	0.120	20	36.3
DAL	3DAL20002	2010	135	24	1.3	3.3	26.0	36	31.00	< 0.250	100	180.0
DAL	3DAL20004	1995	100	11.3	0.80	0.31	16.4	11.9	27.5	0.528	34.0	82.3
DAL	3DAL20004	2000	95	9.1	0.32	0.16	16.2	14.1	20.1	0.070	37.4	< 83.8
DAL	3DAL20004	2005	98	10	0.058	0.854	3.6	3.08	< 9.59	0.056	8.34	20
DAL	3DAL20004	2010	100	16	1.00	2.4	28	19	19	< 0.230	48	120
DAL	3DAL20008	1995	50	12.1	1.10	0.45	25.1	13.5	25.2	0.599	31.6	107
DAL	3DAL20008	2000	50	10.7	0.80	0.21	29.2	15.5	20.5	0.080	33.0	< 113
DAL	3DAL20008	2005	56	11	0.081	0.745	6.9	3.91	< 10	0.135	7.73	28
DAL	3DAL20008	2010	58	12	1.3	2.2	30	17	20	< 0.190	33	120
DAL	3DAL20009	1995	12	6.7	2.30	0.49	17.2	16.1	17	0.644	42.2	133

APPENDIX A
SUMMARY OF CRB SEDIMENT DATA

Reservoir	Station	Sample Year	Sample Depth (feet)	Sediment Concentration, dry weight (mg/kg)										
				As	Be	Cd	Cr	Cu	Pb	Hg	Ni	Zn		
DAL	3DAL20009	2000	15	6.0	1.81	0.39	17.1	16.1	14.1	0.070	51.4	<	141	
DAL	3DAL20009	2005	20	5.45	0.370	0.924	5.8	4.14	<	9.73	0.059	14	41	
DAL	3DAL20009	2010	15	4	0.730	1.1	16.0	6.10	5.40	<	0.070	19	47	
DAL	3DAL20010	1995	15	4.6	0.90	0.43	13.5	8.7	14.6	0.497	22.8	<	63.5	
DAL	3DAL20010	2000	10	6.4	1.00	0.42	31.8	13.6	16	0.060	39.6	<	103	
DAL	3DAL20010	2005	15	6.38	0.174	0.513	8.6	3.30	<	10	0.076	11	27	
DAL	3DAL20010	2010	16	3.6	0.71	0.93	14.0	7.10	12	<	0.090	14	42	
DAL	3DAL20050	1995	60	10.6	1.70	0.53	22.3	16.2	27.7	0.613	57.8	<	138	
DAL	3DAL20050	2000	55	10.4	1.40	0.22	39.1	18.0	24.3	0.080	64.1	<	144	
DAL	3DAL20050	2005	62	23	0.363	1.02	8.6	6.02	7.82	0.075	20	49		
DAL	3DAL20050	2010	62	13	2.1	2.7	36	22	22	<	0.190	69	170	
DAL	3DAL20051	1995	11	5.1	0.60	0.496	14.9	10.2	16.7	0.523	29.3	76.2		
DAL	3DAL20051	2000	15	6.8	0.21	0.35	22.7	12.2	14.4	0.080	34.4	<	93.2	
LAU	3LAU20002	1998	245	8.1	0.92	1.4	19	18	20.9	0.071	32.9	84.8		
LAU	3LAU20002	2003	245	8.1	0.92	1.40	19	18	20.9	0.070	32.9	<	84.8	
LAU	3LAU20002	2008	236	<	8.7	1.00	2.61	21	16.8	27.5	<	0.050	35.2	94.1
LAU	3LAU20005	1998	135	12	1.50	0.29	32.7	27.9	34.8	0.080	54.9	130		
LAU	3LAU20005	2003	145	11	1.40	1.40	25.2	31.1	27.4	0.080	34.4	<	139	
LAU	3LAU20005	2008	138	<	15	1.30	2.50	25.2	24.8	26.2	<	0.050	33.4	117
LAU	3LAU20006	1998	175	3.5	0.80	0.05	17	9.3	14.5	0.048	17.7	51.7		
LAU	3LAU20006	2003	175	7.8	1.10	1.30	19	21	21.2	0.080	29.2	<	85.6	
LAU	3LAU20006	2008	172	<	10	0.90	2.10	20	17.5	24	<	0.050	29	76
LAU	3LAU20007	1998	22	5.1	0.80	0.34	21.5	44.7	28.1	0.088	23.3	130		
LAU	3LAU20007	2003	30	5.1	0.93	1.20	17	30.5	22.3	0.090	24.8	<	171	
LAU	3LAU20007	2008	28	<	7	0.90	1.76	19.1	37.9	25.9	<	0.050	28.3	184
MAR	3MAR20002	1997	35	3.1	1.10	0.31	7.6	21.2	19.3	0.059	31.7	82.7		
MAR	3MAR20002	2002	32	7.3	1.58	0.903	19.8	29.2	20.3	0.055	44.6	153	B	
MAR	3MAR20002	2007	33	1.6	1.39	4.860	19.3	27.9	26.4	<	0.240	34.4	135	
MAR	3MAR20004	1997	9	1.8	0.80	0.230	4.6	11.1	28.7	0.035	9.7	41.4		
MAR	3MAR20004	2002	10	4.1	0.96	0.646	11.6	16.3	14.3	0.041	20.1	82.6	B	
MAR	3MAR20004	2007	10	1.8	1.07	3.630	15.6	23.8	20.7	<	0.240	24.1	107	
MAR	3MAR20005	1997	24	2.3	0.8	0.270	6.7	17.3	15.8	0.045	24.1	66.2		
MAR	3MAR20005	2002	22	5.7	1.22	0.756	17.4	23.1	16.9	0.043	36	120	B	
MAR	3MAR20005	2007	23	1.7	1.38	4.9	19.9	25.4	26.7	<	0.240	35.7	137	
MAR	3MAR20006	1997	4	2.4	0.8	0.170	0.5	13.8	11.2	0.036	16.3	47.3		
MAR	3MAR20006	2002	18	6.6	1.28	0.801	17.5	26.2	17.1	0.045	35.8	126	B	
MAR	3MAR20006	2007	10	2	0.84	2.850	11.6	20.2	16.3	<	0.240	12	44	
WOL	3WOL20002	1998	160	13	1.2	0.4	24	23.9	26.4	0.082	58	122		
WOL	3WOL20002	2003	160	14	1.2	1.5	24	26	20	0.076	63	146		
WOL	3WOL20002	2008	140	<	10	0.7	1.33	15	14.2	12.3	<	0.050	39.7	78.8
WOL	3WOL20004	1998	134	11.9	1.6	0.39	26.3	26.3	32.9	0.087	59	145		
WOL	3WOL20004	2003	135	12	1.6	1.5	27	29	26	0.079	56	161		
WOL	3WOL20004	2008	114	<	10	1.1	1.69	20.5	18.2	18.9	<	0.050	40.4	101
WOL	3WOL20006	1998	80	8	1.4	0.3	22	23	26	0.100	43	127		
WOL	3WOL20006	2003	98	8	1.3	1.40	22	27	22	0.059	42	145		
WOL	3WOL20006	2008	71	<	7.6	1.3	2.06	23.5	23.1	0.050	41	125		
WOL	3WOL20007	1998	95	9	1.6	0.3	25	24	25	0.100	48	131		
WOL	3WOL20007	2003	98	8.4	1.5	1.5	25	25	21	0.063	44	143		
WOL	3WOL20007	2008	72	<	7.8	1.2	1.82	22.5	18.5	18.3	<	0.050	35	106
WOL	3WOL20010	1998	80	8	1	0.59	22	16.4	28.8	0.102	22.1	98		
WOL	3WOL20010	2003	25	7.8	0.76	1.3	22	13	22	0.080	15	93		
WOL	3WOL20010	2008	72	<	10	0.50	1.27	20.2	12.3	20	<	0.050	12.4	81.5
WOL	3WOL20011	1998	52	7.9	1	0.39	17	13.9	20.8	0.076	44.4	96.4		
WOL	3WOL20011	2003	50	4.6	0.06	0.76	17	13	17	0.056	28	102		
WOL	3WOL20011	2008	29	<	8.4	0.80	1.56	21.4	12.9	17	<	0.050	32.8	87.5
WOL	3WOL20047	1998	22	4.7	0.70	0.20	20	11.4	22	0.802	21.8	84.8		
WOL	3WOL20047	2003	20	7.8	0.08	1.20	20	15	17	0.059	41	101		
WOL	3WOL20047	2008	12	<	4.1	0.40	0.791	10.7	10.8	14.8	<	0.050	15.2	64.3

APPENDIX A SUMMARY OF CRB SEDIMENT DATA

Reservoir	Station	Sample Year	Sample Depth (feet)	Sediment Concentration, dry weight (mg/kg)													
				As	Be	Cd	Cr	Cu	Pb	Hg	Ni	Zn					
CHE	3CHE2002	1994	40	1.5	<	0.59	<	1.47	3.8	2.6	9.6	0.100	6.1	<	25.5		
CHE	3CHE2002	1999	40	3.9		0.4		0.13	9.9	0.2	10.7	<	0.040		6.7	22.7	
CHE	3CHE2002	2004	38	2.54		0.308	<	0.480	6.9	3.74	10	0.022	7.49		31		
CHE	3CHE2002	2009	39	4.30		0.690		1.2	14	9.20	15	<	0.090		16	77	
CHE	3CHE2005	1994	25	1.3	<	0.74	<	1.84	2.7	18.2	19.9		0.080	7.5	<	49.5	
CHE	3CHE2005	1999	20	5.7		0.70		0.44	16.9	11	20.7		0.064	17.6		69.5	
CHE	3CHE2005	2004	17	<	4.34	0.321	<	0.434	5.5	4.53	5.8		0.018	8.67		23.1	
CHE	3CHE2005	2009	20	3.40		0.610		1.1	12	9.60	15.0	<	0.090	15		77	
CHE	3CHE2008	1994	20	1.0	<	0.60	<	1.51	<	1.8	5.9		0.060	3.1	<	21.7	
CHE	3CHE2008	1999	20	4.8		0.70		0.16	17.5	9.8	22.8		0.084	15.4		50	
CHE	3CHE2008	2004	5	<	4.41	0.361	<	0.441	7.7	6.03	32		0.049	8.94		32	
CHE	3CHE2008	2009	8	3.70		0.430		0.940	9.8	5.30	15	<	0.070	12		42	
CHE	3CHE2012	1994	26	0.8	<	0.80	<	2	3.3	6.5	16.1		0.25	5.1	<	23.3	
CHE	3CHE2012	1999	29	5.5		1.00		0.40	23.4	10.1	22.5		0.058	18.1		62.3	
CHE	3CHE2012	2004	25	<	4.70	0.282	<	0.470	5.7	4.10	7.65		0.022	5.62		24	
CHE	3CHE2012	2009	25	5.20		0.810		1.5	22	6.20	10	<	0.090	14		51	
CHE	3CHE20038	1994	17	1.4	<	0.61	<	1.54	2.3	5.9	15.3	<	0.070	6.3	<	37.3	
CHE	3CHE20038	1999	6	5.4		0.60		0.13	12.4	6.3	11.7		0.040	11.4	<	46.4	
CHE	3CHE20038	2004	3	<	6.57	0.460		0.184	9.7	7.60	13		0.040	12		52	
CHE	3CHE20038	2009	10	5.30		0.770		1.800	12.0	7.20	11	<	0.070	17		44	
CHE	3CHE20080	1994	19	2.0	<	1.01	<	2.54	<	3.0	9.7	<	0.110	3.8	<	35.7	
CHE	3CHE20080	1999	20	5.4		0.80		0.41	20.6	10	19.4		0.048	17		60.4	
CHE	3CHE20080	2004	17	<	4.89	0.293	<	0.489	7.2	5.64	9.37		0.023	7.36		31	
CHE	3CHE20080	2009	12	5.30		0.900		1.500	21	11	19.00	<	0.140	18		81	
CHE	3CHE20081	1994	12	1.8	<	0.59		3.14	5.6	18.7	42.4	<	0.070	11.2	<	76.9	
CHE	3CHE20081	1999	9	8.1		1.20		1.12	28.6	33.3	62.8		0.100	24.8		212	
CHE	3CHE20081	2004	10	<	4.40	0.299	<	0.440	6.7	7.25	24		0.018	8.54		47	
CHE	3CHE20081	2009	8	3.10		0.430		1.500	9.6	4.70	26	<	0.080	10		170	
CHE	3CHE20082	1994	12	3.1	<	0.73		3.55	20.7	19.6	39.4		0.220	15.0	<	68.1	
CHE	3CHE20082	1999	15	9.8		1.20		0.39	26.2	18.0	25.1		0.064	27.1		88.1	
CHE	3CHE20082	2004	13	1.60		0.310	<	0.470	6.7	7.61	11		0.025	8.41		41	
CHE	3CHE20082	2009	12	9.20		1.300		2.400	25	23	26	<	0.140	30		130	
CHE	3CHE20083	1994	13	2.5	<	0.56		3.65	9.1	2.7	21.8		0.070	3.0	<	35.5	
CHE	3CHE20083	1999	10	5.2		1.10		0.33	23.6	15.1	31.7		0.084	15.8		122	
CHE	3CHE20083	2004	5	<	4.18	0.284	<	0.418	4.9	6.06	12		0.029	4.15		50	
CHE	3CHE20083	2009	8	4.30		1.000		1.700	20	20	27	<	0.120	15.00		150	
CHE	3CHE20084	1994	17	1.6	<	0.56		2.37	2.9	7.6	15.9		0.070	9.8	<	28.9	
CHE	3CHE20084	1999	5	8.9		0.90		0.20	20.5	10	18.9	<	0.040	20.9		53.7	
CHE	3CHE20084	2004	4	7.97		0.935		0.295	17	12	28		0.035	19		84	
CHE	3CHE20084	2009	4	25		1.300		2.800	21	10	20	<	0.060	25		71	
CHE	3CHE20085	2004	5	<	4.89	0.274	<	0.489	4.9	5.55	12		0.031	4.11		59	
JPP	3JPP20002	1994	95	4.9	<	2.04		8.16	14.6	<	5.1	40.7	<	0.150	20.2	<	83.3
JPP	3JPP20002	1999	95	6.8		1.30		0.18	24.2	14.4	26.2		0.064	17.4		53.7	
JPP	3JPP20002	2004	96	25		0.826	<	2.43	21.8	18	32		0.066	13		96	
JPP	3JPP20002	2009	96	6		1.600		1.90	25	20	23	<	0.370	22		84	
JPP	3JPP20003	1994	75	3.3	<	1.10		6	13.6	<	2.8	39	<	0.100	15.5	<	74.2
JPP	3JPP20003	1999	74	6.3		1.40		0.19	29.0	14.3	28.9		0.064	21		64.2	
JPP	3JPP20003	2004	75	7.33		0.203	<	0.441	4.7	3.85	5.9		0.015	3.59		20	
JPP	3JPP20003	2009	80	3.5		1.2		1.4	20	14	17	<	0.320	16		78	
JPP	3JPP20004	1994	15	3.27		1.07		6.2	18.3	16.6	45.8	<	0.100	24.4		109	
JPP	3JPP20004	1999	13	5.7		1.20		0.279	22.6	15.3	23.4		0.068	18.9		63.5	
JPP	3JPP20004	2004	15	5.61		0.243	<	0.434	5.7	6.26	8.5		0.029	4.46		44	
JPP	3JPP20004	2009	16	2.10		1.0		1.200	15	14	15	<	0.200	14		98	
JPP	3JPP20005	2009	28	2.70		1.1		1.400	17	16	17.0	<	0.220	17		89	
JPP	3JPP20006	1994	18	4.9		1.79		9.7	37.5	34	84.4		0.220	33.9		183	
JPP	3JPP20006	1999	16	6.0		1.30		0.689	66.2	6.8	29.2		0.070	16.6		65.4	
JPP	3JPP20006	2004	18	7.35		0.529	<	0.490	25	4.38	17		0.030	7.77		40	
JPP	3JPP20006	2009	22	1.80		1.0		1.200	17	14	17	<	0.200	12		92	
JPP	3JPP20007	1994	20	6.2		1.84		10.6	26	28.2	67.7	<	0.160	46.0		142	
JPP	3JPP20007	1999	19	5.4		1.10		0.28	26.8	11.7	21.7		0.060	19.7		52.4	
JPP	3JPP20007	2004	22	5.46		0.29	<	0.49	8.33	5.85	8.01		0.02	5.99		26	
JPP	3JPP20007	2009	25	7.5		1.3		2.4	19.0	13.0	16	<	0.230	21		69	
JPP	3JPP20008	1994	46	5		1.53		8.55	20.3	23.3	55	<	0.120	26.8		101	
JPP	3JPP20008	1999	45	4		1		0.3	21.2	12.9	21.3		0.064	15.8		70.8	
JPP	3JPP20008	2004	45	5.49		0.256	<	0.491	6.5	5.40	8.4		0.022	5.19		27	
JPP	3JPP20008	2009	46	2.60		1		1.3	16	13	14	<	0.210	14		66	
JPP	3JPP20009	1994	37	6.2		1.79		10.2	30.7	25.8	76.8	<	0.160	30.4		130	
JPP	3JPP20009	1999	41	6.2		1.40		0.21	29.2	16.4	27.5		0.064	21.3		68.2	
JPP	3JPP20009	2004	50	7.29		0.235	<	0.436	6.2	4.60	7.3		0.019	3.97		23	
JPP	3JPP20009	2009	55	2		0.940		1.200	17	12	14	<	0.260	13		81	
JPP	3JPP20010	1994	26	2.0		1.34		5.94	15.5	2.8	40		0.100	18.1		81.8	

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Reservoir	Station	Sample Year	Sample Depth (feet)	Sediment Concentration, dry weight (mg/kg)									
				As	Be	Cd	Cr	Cu	Pb	Hg	Ni	Zn	
JPP	3JPP20010	1999	21	2.8	0.80	0.17	17	9.5	21.2	0.060	11.1	40.5	
JPP	3JPP20010	2004	23	4.08	0.163	< 0.430	4.7	3.66	6.3	0.026	3	NA	J
JPP	3JPP20010	2009	35	1.40	0.890	1.0	16	11	15	< 0.26	11	60	
JPP	3JPP20011	2009	35	2.50	1.300	1.4	20	14	18	< 0.27	15	91	
JPP	3JPP20012	2009	17	2.10	1.200	1.4	17.0	13	18	< 0.23	14	57	
OLD	3OLD20002	1996	71	6.4	1.10	0.52	17.4	21.4	20.9	< 0.10	29.1	93.2	
OLD	3OLD20002	2001	70	7.0	1.20	0.26	17.5	21.4	20.8	0.08	29.9	95.3	B
OLD	3OLD20002	2006	64	8.1	0.90	< 0.30	17.0	15.0	18.0	0.24	27	87	
OLD	3OLD20005	1996	50	5.0	0.70	0.30	11.4	8.8	11.4	< 0.10	17.2	56	
OLD	3OLD20005	2001	45	5.9	0.88	0.23	12.1	14.8	14.0	0.06	19.8	68.1	B
OLD	3OLD20005	2006	51	5.4	0.77	< 0.26	13	13	15	0.31	21	69	
OLD	3OLD20007	1996	8	4.2	0.60	0.19	10.4	5.5	9.4	< 0.10	13.7	< 41.7	
OLD	3OLD20007	2001	40	7.5	1.00	0.23	13.5	12.9	17.6	0.06	23.8	76.7	B
OLD	3OLD20007	2006	71	6.5	0.87	0.22	14	11	15	0.16	23	74	
OLD	3OLD20013	1996	29	7.8	1.3	0.28	19.1	21.9	25	< 0.1	27.4	88.2	
OLD	3OLD20013	2001	26	8.1	1.4	< 0.50	18	17.2	20.2	0.059	24.8	73.9	B
OLD	3OLD20013	2006	26	9.2	1.3	< 0.42	21	21	25	0.420	27	97	
OLD	3OLD20018	1996	28	5.9	1.4	0.331	19.6	22.6	24.8	< 0.100	23.7	85.9	
OLD	3OLD20018	2001	23	9	1.5	< 0.5	18.6	21.6	22.2	0.069	22	86.3	B
OLD	3OLD20018	2006	23	< 8.5	1.3	< 0.43	22	21	26	0.26	25	102	
OLD	3OLD20020	1996	36	8	1.1	0.38	17.6	23.5	22.8	< 0.10	27.2	87.7	
OLD	3OLD20020	2001	23	7.7	1.3	0.15	18.2	25.2	20.7	0.075	27.5	98.3	B
OLD	3OLD20020	2006	21	< 6.9	1.0	< 0.35	18	17	21	0.23	25	87	
OLD	3OLD20021	1996	17	4	1.2	0.51	18.3	18.2	27.8	< 0.10	15.1	97.8	
OLD	3OLD20021	2001	20	5	1.4	0.23	18.3	17.5	24.8	0.086	18	93.2	B
OLD	3OLD20021	2006	20	< 6.7	1	< 0.34	19	13	23	0.22	18	100	
OLD	3OLD20022	1996	22	6.1	1	0.35	13.9	17.5	17.4	< 0.100	24.2	68	
OLD	3OLD20022	2001	24	6.5	1.20	0.19	15.2	18.2	19.2	0.06	26.4	78.5	B
OLD	3OLD20022	2006	24	6.9	0.94	< 0.31	16	16	19	0.200	24	75	
N:				227	227	227	227	227	227	227	227	226	
Nondetects:				23	14	34	2	2	6	78	0	31	
% Nondetect:				10.13	6.17	15	0.881	0.881	2.643	34.36	0	13.7	
USGS Mean Baseline:				8.1	1.6	0.5	66	24	24	0.08	28	100	

NOTES:
 NA=Not analyzed; Less than (<)=Not detected at reporting detection limit; J=estimated value, assumed less than contract required quantification limit (CRQL), but greater than or equal to method detection limit (MDL); B=found in blank.
Bold=Outlier, per ProUCL assume ND equal to detection limit.
 Shaded=exceeds USGS mean baseline concentration.

REFERENCES

- ATSDR (Agency for Toxic Substances and Disease Registry), 2011. <http://www.atsdr.cdc.gov/>.
- Brigham, M. E., Krabbenhoft, D. P., and P.A. Hamilton, 2003. Mercury in stream ecosystems -- new studies initiated by the U.S. Geological Survey. Fact Sheet 016-03, <http://pubs.usgs.gov/fs/fs-016-03/>.
- Brown, L.R., Cuffney, T.F., Coles, J.F., Fitzpatrick, F., McMahon, G., Steuer, J., Bell, A.H., and J.T May, 2009. Urban streams across the USA: lessons learned from studies in nine metropolitan areas. *Journal of the North American Benthological Society*, 28(4):1051–1069.
- Callendar, E. and K. C. Rice, 2000. The urban environmental gradient: anthropogenic influences on the spatial and temporal distributions of lead and zinc in sediments. *Environmental Science & Technology*, 34(2): 232-238.
- Chalmers, A.T., Van Metre, P.C., and E. Callendar, 2007. The chemical response of particle-associated contaminants in aquatic sediments to urbanization in New England, U.S.A. *Journal of Contaminant Hydrology*, 91 (2007) 4–25.
- Chapman, P.M., Wang, F., Janssen, C.R., Goulet, R.R, and C.N. Kamunde, 2003. Conducting ecological risk assessments of inorganic metals and metalloids: current status. *Human and Ecological Risk Assessment*, 9 (4): 641-697.
- Council T.B., Duckenfield, K.U., Landa, E.R., and E. Callender, 2004. Tire-wear particles as a source of zinc to the environment. *Environmental Science & Technology*, 38:4206–4214.
- de Smith, M.J., Goodchild, M.F., and P.A. Longley, 2006. Geospatial analysis: a comprehensive guide to principles, techniques and software tools, third edition, <http://www.spatialanalysisonline.com/>.
- ESRI, 2008. ArcGIS 9.3 Data and Maps. CD of geospatial data accompanying ArcView 9.3 license.
- Gilbert, R.O., 1987. Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold, New York.
- Gleick, P.H., 2003. Global freshwater resources: soft-path solutions for the 21st century. *Science*, 302:1524-1528.
- Helsel, D.R., 1990. Less than obvious: statistical treatment of data below the detection limit. *Environmental Science & Technology*, 24(12):1766–74.

- Helsel, D.R., 2005. More than obvious: better methods for interpreting nondetect data. *Environmental Science & Technology*, 39 (20), 419A–423A.
- Helsel, D.R., 2010. Much ado about next to nothing: incorporating nondetects in science, *Annals of Occupational Hygiene*, 54(3): 257–262.
- Hollister, J.W., August, P.V., and J. F. Paul, 2008. Effects of spatial extent on landscape structure and sediment metal concentration relationships in small estuarine systems of the United States' Mid-Atlantic Coast. *Landscape Ecology*, 23:91–106.
- Hornberger, G.M., Raffensperger, J.P., Wiberg, P.L., and K.N. Eshleman, 1998. Elements of Physical Hydrology. The Johns Hopkins University Press.
- Horowitz, A.J. and V.C Stephens, 2008. The effects of land use on fluvial sediment chemistry for the conterminous U.S.: Results from the first cycle of the NAWAQ program: trace elements, phosphorus, carbon, and sulfur. *Science of the Total Environment*, 400:290-314.
- KDEP (Kentucky Department of Environmental Protection), 2008. *Final 2008 Integrated Report to Congress on the Condition of Water Resources in Kentucky, Volume II., 303(d) List of Surface Waters*, <http://water.ky.gov/waterquality/303d%20Lists/2008volume2final.pdf>.
- MacDonald D.D., Ingersoll C.G., Berger T.A., 2000. Development and evaluation of consensus-based quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology*, 39:20–31.
- MacDonald, D.D. and C. G. Ingersoll, 2002. *A Guidance Manual to Support the Assessment of Contaminated Sediments in Freshwater Ecosystems, Volume II – Design and Implementation of Sediment Quality Investigations*, EPA-905-B02-001-B, for the U.S. Environmental Protection Agency, Great Lakes National Program Office, <http://www.epa.gov/greatlakes/sediment/Vol2.pdf>.
- Mahler, B.J., P.C. Van Metre, and E. Callendar, 2006. Trends in metals in urban and reference lake sediments across the United States, 1970 to 2001. *Environmental Toxicology and Chemistry*, 25(7):1698–1709.
- McGrew J. C. and C.B. Monroe, 2000. An Introduction to Statistical Problem-Solving in Geography, 2nd edition. McGraw Hill, Boston.
- Mitchell, A., 1999. The ESRI Guide To GIS Analysis, Volume I: Geographic Patterns And Relationships. ESRI Press, Redlands, CA.

Moltz, H.L., Rast, W., Lopes, V.L., and S.J. Ventura, 2011. Use of spatial surrogates to assess the potential for non-point source pollution in large watersheds, *Lakes & Reservoirs: Research and Management*, 16:3-13.

MRLC (Multi-Resolution Land Cover Consortium), 2011. National land cover dataset, 2006
<http://www.mrlc.gov/nlcd2006.php>.

Novotny, V., and H. Olem, 1994. Water Quality: Prevention, Identification, and Management of Diffuse Pollution. Van Nostrand Reinhold, New York.

Ongley, E. D., 1996. Chapter 13, Sediment Measurements, *IN: Water Quality Monitoring: A Practical Guide To The Design And Implementation Of Freshwater Quality Studies and Monitoring Programmes*, pages 317-332, United Nations Environment Programme and the World Health Organization. Bartram, J. and R. Ballance (eds).

Paul, M.J. and J.L. Meyer, 2001. Streams in the urban landscape. *Annual Review of Ecology, Evolution, and Systematics*, 32: 333–65.

Percival, R.V., Schroeder, C.H., Miller, A.S., and J.P. Leape (eds.), 2009. Environmental Regulation: Law, Science, and Policy, 6th edition, Aspen Publishing, Wolters Kluwer, Austin, Texas.

Rice, K.C., 1999. Trace-element concentrations in streambed sediment across the conterminous United States. *Environmental Science & Technology*, 33: 2499-2504.

Rijsberman, F.R., 2006. Water scarcity: fact or fiction? *Agricultural Water Management*, 80:5-22.

Roy, A.H., Dybas, A.L., Fritz, K.M., and H.R. Lubbers, 2009. Urbanization affects the extent and hydrologic permanence of headwater streams in a midwestern US metropolitan area. *Journal of the North American Benthological Society*, 28(4):911–928.

Singh, A., 2006. *On the Computation of a 95% Upper Confidence Limit of the Unknown Population Mean Based Upon Data Sets with Below Detection Limit Observations*, EPA/600/R-06/022, <http://www.epa.gov/esd/tsc/appendix/EPA600R-06-022.pdf>.

Sneed, R., 2006. Personal Communication with L. Benneyworth and Robert Sneed of USACE, Nashville District.

Sneed, R., 2011. Personal Communication with L. Benneyworth and Robert Sneed of USACE, Nashville District.

TDEC (Tennessee Department of Environmental Conservation), 2010. *Draft 2010 303 (d) List, May 2010*, www.state.tn.us/environment/water.shtml.

Tippit, R. and M. Campbell, 2011. Personal Communication with L. Benneyworth, Richard Tippit, and Mark Campbell of USACE, Nashville District.

UNEP (United Nations Environment Programme), 1999. Division of Technology, Industry and Economics. Newsletter and Technical Publications. Planning and management of lakes and reservoirs: an integrated approach to eutrophication (TP-11), <http://www.unep.or.jp/ietc/Publications/techpublications/TechPub-11/>.

UNEP (United Nations Environment Programme), 2000. Division of Technology, Industry and Economics. Newsletter and Technical Publications Short Series. Lakes and reservoirs - similarities, differences and importance (SS-1), http://www.unep.or.jp/ietc/publications/short_series/lakereservoirs-1/index.asp.

USACE (U.S. Army Corps of Engineers), 1994. USACE guidance #1110-2-26, *Water Quality Investigations and Control Activities*. [not available online]

USACE (U.S. Army Corps of Engineers), 1996. *Operational Assessment, Cumberland River Basin*, Ohio River Division, Nashville District. [not available online]

USACE (U.S. Army Corps of Engineers), 2010. *After Action Report: May 2010 Flood Event, Cumberland River Basin, 1-3 May 2010*, Great Lakes and Ohio River Division, http://www.orn.usace.army.mil/LRN_pdf/AAR/LRN%20AAR%20Final.pdf

U.S. Census Bureau, 2002. *Federal Register*, 67(84): 21962-21967, May 1, 2002.

U.S. Census Bureau, 2011. Census 2000, urban and rural classification, http://www.census.gov/geo/www/ua/ua_2k.html.

USDOE (U.S. Department of Energy), 1996. Toxic substances from coal combustion: a comprehensive assessment. *Quarterly Report 7/1/96 to 9/30/96*, PSI-1245, DOE/PC/95101-T4.

USEPA (U.S. Environmental Protection Agency), 1989. *Risk Assessment Guidance for Superfund Volume I, Human Health Evaluation Manual (Part A), Interim Final*, EPA/540/1-89/002, <http://www.epa.gov/oswer/riskassessment/ragsa/pdf/preface.pdf>.

USEPA (U.S. Environmental Protection Agency), 1994. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846*, as revised 2007, <http://www.epa.gov/epawaste/hazard/testmethods/sw846/index.htm>.

USEPA (U.S. Environmental Protection Agency), 1997. *The Incidence and Severity of Sediment Contamination in Surface Waters of the United States, volume 1-National Sediment Survey*, EPA-823-R-97-006, http://water.epa.gov/polwaste/sediments/cs/report1997_index.cfm.

USEPA (U.S. Environmental Protection Agency), 2002. *National Water Quality Inventory: 2000 Report to Congress*, EPA-841-R-02-001, nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=20004R2T.txt

USEPA (U.S. Environmental Protection Agency), 2004. *The Incidence and Severity of Sediment Contamination in Surface Waters of the United States, 2nd ed.*, EPA-823-R-04-007, http://water.epa.gov/polwaste/sediments/cs/report2004_index.cfm.

USEPA (U.S. Environmental Protection Agency), 2005. *National Management Measures to Control Nonpoint Source Pollution from Urban Areas*, EPA-841-B-05-004, http://www.epa.gov/owow/NPS/urbanmm/pdf/urban_guidance.pdf.

USEPA (U.S. Environmental Protection Agency), 2009a. *National Lakes Assessment: A Collaborative Survey of the Nation's Lakes*, EPA 841-R-09-001, http://www.epa.gov/owow/LAKES/lakessurvey/pdf/nla_chapter0.pdf.

USEPA (U.S. Environmental Protection Agency), 2009b. *Characterization of Coal Combustion Residues from Electric Utilities – Leaching and Characterization Data*, EPA-600/R-09/151, <http://www.epa.gov/nrmrl/pubs/600r09151/600r09151.pdf>.

USEPA (U.S. Environmental Protection Agency), 2009c. *National Water Quality Inventory: 2004 Report to Congress*, EPA 841-R-08-001, http://www.epa.gov/owow/305b/2004report/2004_305Breport.pdf.

USEPA (U.S. Environmental Protection Agency), 2010. *ProUCL Version 4.1 User Guide (Draft): Statistical Software for Environmental Applications for Data Sets With and Without Nondetect Observations*, EPA/600/R-07/041, http://www.epa.gov/osp/hstl/tsc/ProUCL_v4.1_user.pdf.

USEPA (U.S. Environmental Protection Agency), USEPA, 2011a. Water Quality Assessment and Total Maximum Daily Loads Information, Watershed Assessment, Tracking & Environmental Results (WATERS), <http://www.epa.gov/waters/ir/>.

USEPA (U.S. Environmental Protection Agency), USEPA, 2011b. ProUCL Webinar, ORD Site Characterization and Monitoring Technical Support Center. Part 1 (3/9/11), http://www.clu-in.org/conf/tio/ProUCLBasic_030911/; and Part 2 (3/16/11), http://www.clu-in.org/conf/tio/ProUCLAdv_031611/.

USEPA (U.S. Environmental Protection Agency), USEPA, 2011c. ProUCL Version 4.1.00 Technical Guide, Draft. EPA/600/R-07/041, http://www.epa.gov/osp/hstl/tsc/ProUCL_v4.1_tech.pdf.

USEPA (U.S. Environmental Protection Agency), USEPA, 2011d. Online Geospatial Database updated April 2011, http://www.epa.gov/enviro/geo_data.html.

USGS (U.S. Geological Survey), 2009. *Derivation of Nationally Consistent Indices Representing Urban Intensity Within and Across Nine Metropolitan Areas of the Conterminous United States*, Scientific Investigations Report 2008-5095, <http://pubs.usgs.gov/sir/2008/5095/>.

USGS (U.S. Geological Survey), 2011. Sampling trace elements in urban environmental settings, National Water Quality Assessment Program. http://co.water.usgs.gov/nawqa/urbanPortal/html/traceelements_urban.html.

Van Metre P.C., Mahler B.J., 2003. The contribution of particles washed from rooftops to contaminant loading to urban streams. *Chemosphere*, 52:1727–1741.

Van Metre, P. C. and B. J. Mahler, 2004. Contaminant trends in reservoir sediment cores as records of influent stream quality. *Environmental Science & Technology*, 38(11):2978-2984.

WES (U.S. Army Engineer Research and Development Center, Waterways Experiment Station), 1998. *The WES Handbook on Water Quality Enhancement Techniques for Reservoirs and Tailwaters*, <http://chl.ercd.usace.army.mil/chl.aspx?p=s&a=Publications!26>.

