SOURCES OF LEAD TO THE SEDIMENTS AND FLOODPLAIN DEPOSITS OF THE BIG RIVER

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ACRONYMS AND ABBREVIATIONS

cfs	cubic feet per second
Doe Run	The Doe Run Resources Corporation
EPA	U.S. Environmental Protection Agency
MDNR	Missouri Department of Natural Resources
MR&BT	Mississippi River and Bonne Terre Railway
myd^3	million cubic yards
NPL	National Priorities List
PEC	preliminary effects concentration
RM	river mile
SFCMA	St. Francois County Mining Area
St. Joe	St. Joe Minerals Corporation
TMDL	total maximum daily load
USGS	U.S. Geological Survey
WCLD	Washington County Lead District
yd^3	cubic yards

EXECUTIVE SUMMARY

This report identifies the sources of metals that are currently present in the sediments and floodplain deposits of the Big River and provides a preliminary assessment of the magnitude of different source contributions. The primary sources of metals include the following:

- Mining operations on the Upper Big River
- Mining operations on Flat River Creek
- The SE Missouri Barite District
- The Washington County Lead District
- The Furnace Creek and Valle Mines mining areas
- Historical surface mining, milling, roasting, and smelting (pre-1860s) throughout the Big River watershed
- Erosion of the Bonneterre formation by the Big River and its tributary creeks, and erosion of soils with naturally elevated lead concentrations to form sediments in the Big River
- The Desloge tailings release of July 1977
- Releases of chat, which was used for railroad ballast, to the Big River and its tributaries.

Two major mining districts exist in the Big River watershed: the area that is now called the St. Francois County Mining Area (SFCMA), located in St. Francois County, and the SE Missouri Barite District, located in northeast Washington County and southwest Jefferson County (Figure 1-1). Within the SFCMA, differences in the character of the ore and milling byproducts provide the means to discriminate between contributions from lead sources located on Flat River Creek and sources located on the upper Big River. Likewise, in the SE Missouri Barite District, there are differences in the character of the ore and milling byproducts that allow the discrimination of lead contributions from the SE Missouri Barite District and the SFCMA. A variety of allocation techniques were investigated, including metal concentration profiles, metal ratios, source mixing models, and results from a watershed model that was used to estimate background lead concentrations in Big River sediments. Results of these analyses, in combination with documentation of historical mining practices, indicate that mining operations on Flat River Creek and the upper Big River contributed about equally to lead concentrations in sediments downstream of their confluence, that the SE Missouri Barite District is the primary lead source to the lower Big River, and that naturally mineralized soils contribute significant lead mass to the entire Big River.

1 INTRODUCTION

The Big River watershed has a long history of mineral extraction, and studies have identified past mining as a major source of lead to the Big River watershed. Mining occurred throughout the watershed and was primarily located in two major districts: the areas that are now called the St. Francois County Mining Area (SFCMA) and the SE Missouri Barite District (Figure 1-1). The SFCMA includes seven distinct mine/mill sites located in St. Francois County within the upper Big River watershed (Figure 1-2).[1] Extensive underground lead and zinc mining, and milling, roasting, and smelting operations took place in the SFCMA from the late-1800s until the mid-1970s. Prior to this, historical surface mining occurred throughout St. Francois County, starting in the 1720s and continuing through the advent of underground mining in the late-1800s. Figure 1-3 shows areas where surficial mining is documented to have occurred as of 1824 (the manner in which these areas were identified is discussed in Section 2.4) and parcels of land that were identified by the U.S. government as containing surficial lead ore (as is indicated in American State Papers [1826]). Located primarily in Washington County, Missouri, in the center of the Big River watershed, the SE Missouri Barite District was initially mined for lead ores (1720s to 1880s) and subsequently for barium (1860s to 1990s), and is now the location of multiple National Priorities List (NPL) sites (Figure 1-1).

This report reviews the most significant metals sources to the Big River watershed and discusses the mining and milling operations and ownership history of mines in the SFCMA and SE Missouri Barite District (Section 2). In addition, this report presents an analysis of existing metals concentration data to support quantitative evaluations of lead source contributions (Section 3), and provides a semi-quantitative allocation of lead contributions to the Big River watershed (Section 4).

For the purposes of this report, the term "upper Big River" is defined as the Big River above the confluence with Flat River Creek. The term "middle Big River" is defined as the Big River between the Flat River Creek confluence and where Mill Creek enters the Big River, and the term "lower Big River" is defined as the Big River below the confluence with Mill Creek (Figure 1-1).

[1] The mine/mill and milling-related materials at the Town of Doe Run are not considered in this study because they are located outside the Big River watershed (see Figure 1-2).

2 LEAD SOURCES

2.1 SFCMA MINING SITES

The SFCMA comprises eight identified mining and milling sites, seven of which are located in the Big River watershed (FluorDaniel 1995; Figure 1-2). The following section provides a brief description of the ownership and operational history of these seven locations; the site at the Town of Doe Run is not discussed because it is located outside the Big River watershed (Figure 1-2). The discussion of the sites is subdivided into those located on Flat River Creek and those located on the Big River.

St. Joe Minerals Corporation (St. Joe) which began operations in 1865 was the predecessor to The Doe Run Resources Corporation (Doe Run). St. Joe owned and/or operated the mining and milling operations at the Leadwood, Desloge, and Bonne Terre sites. In contrast, all of the operations on Flat River Creek (Federal, Elvins/Rivermines, and National) were owned and/or operated by other entities for a portion of, or their entire period of operation.

2.1.1 Flat River Creek Sites

This section provides an overview of the operational and ownership history of the three sites located on Flat River Creek: Federal, Elvins/Rivermines, and National.

2.1.1.1 Federal

The first shaft sunk at the Federal site was by the Central Mining Company in 1891 (Fluor Daniel 1995). Other early operators (pre-1905) included the Guggenheim Exploration Co., the Federal Lead Co., the Missouri Smelting Co., and the Catherine Lead Company. All of these companies were either acquired by, or their mines and mills were leased and operated by, the Federal Lead Co. The Federal Lead Co. began operations in 1902 and was controlled by ASARCO (Fluor Daniel 1995).

On October 23, 1923, St. Joe purchased the entire holdings of the Federal Lead Co. As part of this purchase, St. Joe agreed to sell all future concentrates from the mill to ASARCO for smelting. The mill was permanently closed in 1972.

In 1976, St. Joe donated approximately 8,000 acres of the Federal site to the State of Missouri for the creation of St. Joe State Park (Fluor Daniel 1995). Prior to the donation of this property, St. Joe reclaimed the tailings area of the Federal site with a vegetated cover. However, an erosion study in 1995 indicated that approximately 390,000 cubic yards (yd^3) had eroded from the tailings pond during the 19 years between the time the site was donated to the State and the erosion study (Swenty 1995). Eroded tailings were observed in Shaw Branch (Swenty 1995), which drains the Federal tailings pond and discharges to Flat River Creek. In 2007 it was estimated that 10,000 to 30,000 yd^3 of tailings remained in Shaw Branch (NewFields 2007b). Extensive use of all-terrain vehicles at St. Joe Park partially destroyed the vegetated cover, and subsequent erosion resulted in the transport of tailings to Shaw Branch and the Big River.

In summary:

- ASARCO owned the Federal site from 1891 until 1923. This time period is primarily associated with the production of the chat piles because froth flotation milling technology did not became available until the late-1910s. However, ASARCO also produced some tailings during its latter years of operation.
- St. Joe owned the Federal site between 1923 and 1976. This time period is associated with the tailings pond.
- The State of Missouri has owned the site since 1976.

A summary of operations at the Federal site is presented in Table 2-1. NewFields (2006) estimates that there are 5.2 million cubic yards (myd^3) of tailings at the Federal site.

2.1.1.2 Elvins/Rivermines

The first mining operations at this site began in 1890. The historical Doe Run Lead Company, which is a distinct entity from the current Doe Run Resources Corporation, began mining in the Elvins/Rivermines area in 1891 and subsequently acquired the properties and operations of the Columbia Lead Company and Commercial Lead Company. Milling at Elvins was consolidated at one site around 1909 (FluorDaniel 1995) and the mill was permanently closed in about 1934 (NewFields 2006).

The Elvins/Rivermines site was acquired by St. Joe in 1936, subsequent to both the dissolution of the historical Doe Run Lead Company and the shutdown of site operations (NewFields 2006). NewFields (2006) estimates that there are 10.4 myd^3 of chat and tailings at the Elvins/Rivermines site (Table 2-1).

2.1.1.3 National

Mining and milling at the National site commenced in 1894 by the Flat River Lead Co. The National site was purchased by St. Louis Smelting and Refining Co. (a subsidiary of National Lead Co.) in May 1898. St. Louis Smelting and Refining Co. operated a mill at the site to which ore was hauled from various mines in the Flat River Creek area by rail (FluorDaniel 1995). The mill was closed in 1933, after which the property was sold to St. Joe in 1936. Thus, St. Joe never operated the mill (FluorDaniel 1995). The mine continued operation for several years after 1933, during which time ore was shipped underground to the Federal Mill (NewFields 2006). NewFields (2006) estimates that there are 6.4 myd^3 of chat and tailings at the National site (Table 2-1).

2.1.2 Big River Sites

This section provides an overview of the operational and ownership history of the four sites located on the Big River: Leadwood, Desloge, Bonne Terre, and Hayden Creek.

2.1.2.1 Leadwood

St. Joe commenced mining in the Leadwood area in 1894 and began construction of a mill in 1903. Early operations included mining, milling, and roasting. The roasting operations only lasted a few years, with all the furnaces removed between 1908 and 1914. The mill was permanently closed in 1965. NewFields (2006) estimates that there are 5.1 myd^3 of chat and tailings at the Leadwood site (Table 2-1).

2.1.2.2 Desloge

The Desloge Consolidated Lead Company began mining and milling at Desloge in 1887. St. Joe acquired the Desloge site in 1929, and operations at the site continued through 1958, when the mill was permanently closed (FluorDaniel 1995). In 1972, the site was transferred to St. Francois County, and subsequently to the St. Francois County Environmental Corporation (1973) for use as a landfill. In 1977, during a severe storm, approximately 50,000 yd^3 of chat and tailings was released from the southeast edge of the Desloge site to the Big River (FluorDaniel 1995). NewFields (2006) estimates that there are 6.5 myd^3 of chat and tailings at the Desloge site (Table 2-1).

2.1.2.3 Bonne Terre

St. Joe began mining operations at Bonne Terre in 1865. Early operations at the site included mining, milling, roasting, and reverbatory furnace smelting. Smelting of ores at Bonne Terre ceased in 1892, when St. Joe’s Herculaneum smelter became operational (NewFields 2006). The Bonne Terre mill was permanently closed in 1961. NewFields (2006) estimates that there are 5.7 myd^3 of chat and tailings at the Bonne Terre site (Table 2-1).

2.1.2.4 Hayden Creek

St. Joe began mining operations at Hayden Creek in 1951. For the following 3 years, both mining and milling were performed at Hayden Creek. In this deposit, the galena is disseminated in dolomite hosted by a matrix of granitic boulders (USBM 1957). This hard matrix caused difficulties in milling. The mill was shut down in 1954, and ore from Hayden Creek after that time was processed at the Leadwood mill. In 1958 the mine was permanently closed. The volume of tailings at the Hayden Creek site is unknown, but likely very limited considering the short time period of mill operation (Table 2-1).

2.1.3 Chat versus Tailings

Prior to the 1910s, milling in the SFCMA was done by gravity separation using tabling and jigging. This process produced a coarse byproduct referred to as chat, which had been crushed to pass through a 10-mm screen. A sieving analysis of chat indicated that it consisted predominantly of 0.5- to 7-mm material (Watt 1917). This coarse material was disposed of in large piles using conveyors. A small fraction of very fine material, referred to as "slimes," was produced in tandem with the chat. These slimes were disposed of hydraulically, often onto the chat pile. As shown in Figure 2-1, concentrations of lead in chat (data from Wixson et al. 1983) vary between the different SFCMA sites; median values range from 2,180 to 6,000 mg/kg for the different piles.

By 1917, all of the mills in the district had begun using froth flotation for concentrating "fines," typically defined as material <74 µm (i.e., materials passing through a 200 mesh screen) (Watt 1917), while still using tabling and jigging for chat. Over time, the mills transitioned from using froth flotation for the fines only to using froth flotation for all of the crushed ore. This required ore to be milled to smaller particles, with the bulk of material being <250 µm (fine sand, silt, and clay size particles). These milling byproducts are referred to as "tailings" and were disposed of in tailings ponds. As shown in Figure 2-1, median concentrations of lead in tailings (data from Wixson et al. 1983) vary between the different SFCMA sites and range from 720 to 3,250 mg/kg.

2.2 SE MISSOURI BARITE DISTRICT

The SE Missouri Barite District is located in northeast Washington County and southwest Jefferson County (Figure 1-1) and was home to extensive lead and barite mining over a 270-year period (1720s to 1990s) (Figure 2-2). The extent of the SE Missouri Barite District (Figure 1-1) is operationally defined as the area with the highest concentration of lead and/or barium mines.[2] The Washington County Lead District (WCLD), part of which coincides with the SE Missouri Barite District (Figure 1-1), is an area defined by the U.S. Environmental Protection Agency (EPA) that encompasses four separate NPL sites: Richwoods, Potosi, Old Mines, and Furnace Creek. This district is an agglomeration of numerous locations affected by historical mining. In this report, "SE Missouri Barite District" is used to describe the area of historical mining centered in northern Washington County, and "WCLD" is used to denote the conglomeration of the four NPL sites. Given the density of lead and barite mines occurring in this area, the contribution of lead to the Big River watershed has been substantial.

Despite the geographic proximity of the SE Missouri Barite District and the SFCMA, there are substantial differences in geology and mining history between these two mining districts. Early mining activity at the SE Missouri Barite District (1720s to 1880s) focused on the extraction and

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[2] Mine locations identified using the Inventory of Mines, Occurrences and Prospects prepared by the Missouri Department of Natural Resources (MDNR; 2008)

beneficiation of surficial, and near surface, lead ores, while a later mining period (1860s to 1990s) focused on the extraction of surficial barite ores. The heart of the SE Missouri Barite District, which saw the most intense mining activity, comprises an area bounded to the east by the Big River, to the north and west by Mineral Fork, and extending south to the area around Potosi (Figure 2-2). While other areas within Washington County (particularly the Richwoods area to the north of Mineral Fork near the Big River) saw mining activity—this central region is of particular interest because of the combination of a long history of mineral extraction and proximity to the Big River.

Mining of surficial lead ore deposits in the SE Missouri Barite District was extensive and intense, as indicated by the following quotes from the book *Opening the Ozarks* (Schroeder 2002):

> "Because the lead ore occurred over tens of thousands of acres of land, no person could monopolize mining. Should someone seize a miner's pits, the latter could go elsewhere and find more lead…..Naturalist John Bradbury reported that out of forty sites dug in the Richwoods area, thirty-eight contained lead ore. "

Disturbance and denudation of the ground surface during periods of surface mining enhanced sediment transported into streams in the SE Missouri Barite District, which discharged to the Big River. Tarr (1918) describes agricultural bottom lands in the SE Missouri Barite District that were buried under 2 ft of mill tailings, and Schroeder (2002) notes that the surficial mining areas were kept in a state of "perpetual barrenness."

2.2.1.1 Lead Mining in the SE Missouri Barite District

Mining for lead in the SE Missouri Barite District dates back to approximately 1725 with the discoveries of galena at Old Mines and Mine à Renault. The first deposits of galena were found at the surface; later, shallow pits (roughly 10 ft deep) were dug to extract the ore. The galena and co-occurring barite were found in a red clay matrix. In Washington County, these clays vary from a few to several tens of feet in depth. The red clay soils are residual material from the chemical weathering of the underlying bedrock. This weathering results in the galena and barite ore minerals concentrated in the layer of red clay residuum (see Integral 2014 for a discussion of this process). While early mining did not extend deep into the subsurface, the areal extent was significant. One early report noted, in reference to the SE Missouri Barite District, "…this area may be considered as one extensive lead digging, for there is scarcely a township on which there has not been, at some period, more or less mining…" (Swallow 1855). Areas of documented historical surface mining, as shown by the red stippled areas in Figure 1-3, extend throughout St. Francois and Washington counties (the manner by which these areas were established is described in Section 2.4). Additional evidence of the distribution of lead is shown by lands identified by the U.S. government as having lead ore (Figure 1-3).

Production of lead from Washington County between 1740[3] and 1869 amounted to about 78,000 tons (Table 2-2). In the early 1880s, the opening of the mines tapping the disseminated lead deposits of the Bonneterre formation in St. Francois County resulted in a rapid shift away from the surficial lead mines. By the 1920s, the only lead production from the SE Missouri Barite District was as a byproduct of the barite diggings (Dake 1930).

Two primary methods were used for the early smelting of lead ores: the log and ash furnaces, and the Scotch hearth furnace. The earliest mines used log furnaces, in which cleaned ore was roasted for about 24 hours with a large quantity of wood. Recoveries from log furnaces were typically about 50 percent (Schoolcraft 1819; Swallow 1855). The ash furnace was introduced to southeast Missouri in 1799 (Ingalls 1908), and allowed for residual ash from the log furnace to be crushed, washed, and re-roasted, yielding an additional 15 percent lead recovery (Schoolcraft 1819; Swallow 1855). Because of the increased efficiency, the combined log and ash furnace process rapidly supplanted older log furnaces. In 1836, the Scotch hearth furnace was introduced to Missouri (MDNR 1988), and within 20 years, 13 of 14 operating furnaces in Washington County were the Scotch hearth type (Swallow 1855). The Scotch hearth could recover between 70 and 75 percent of the lead from galena ore, with the balance going into the slag and fumes (Middleton 1905). Scotch hearth furnaces required a source of forced air (i.e., the "blast"), which was typically generated by water power. As a result, many of these furnaces were located on streams. Based on these recovery rates, it is estimated that smelting efficiency during the surficial lead mining era was approximately 66 percent. The remaining 34 percent of the lead mass would have been discharged to the soils and creeks of the SE Missouri Barite District.

Early lead mining generated significant volumes of waste due to inefficient extraction and smelting. The efficiency of ore extraction from the lead diggings, using hand sorting and rocker boxes, was approximately 50 percent (Weigel 1953), and the efficiency of smelting, as discussed above, was about 66 percent. Thus, early lead production would have resulted in two tons of lead in waste for every ton of lead metal produced or about 158,000 tons of lead lost to the environment[4] (Table 2-2). A portion of this lead would have been transported to the Big River via tributaries draining surficial lead mining areas. The magnitude of the SE Missouri Barite District as a contributor of lead to the Big River is discussed in Section 3.

2.2.1.2 Barite Mining in the SE Missouri Barite District

Production of barite in Washington County began around 1860 and ceased in 1999; peak production occurred in the 1950s (Figure 2-3; MDNR 2012). Total barite production from the SE Missouri Barite District amounted to approximately 12.7 million tons (MDNR 2012); the extent of surface barite diggings, as estimated by MDNR, is indicated in Figure 1-3. Galena and

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[3] Lead production in Washington County began in 1725 (Winslow 1894).

[4] Calculation based on the documented lead production in Washington County (78,000 tons) and assuming a ore extraction efficiency of 50 percent and a smelting efficiency of 66 percent.

barite were deposited together by the same hydrothermal fluids (Kaiser et al. 1987), and the co-occurrence of barite and galena was so common that early miners used barite as an indicator of lead ore (Schroeder 2002). As with galena, barite was concentrated in the residual, red surface clays that overlay the Eminence and Potosi dolomites throughout the area. Initially, barite was dug by hand and extracted from small pits and shafts. By the early 1940s, the last hand mining operation was closed and mechanized methods were used to extract barite (Wharton 1972). Mechanized operations frequently reworked areas originally hand mined for barite, which, in turn, had originally been hand mined for lead. In the processing of ore, mined material was taken to washing plants where high pressure water jets broke the barite from the gangue; this material was then further sorted and broken before the barite was extracted using gravity jigs. The slurry of water, clay, and rock from the wash plant was discharged into tailings ponds. Post-settling, water from the tailings ponds was re-used as process water or allowed to discharge over the dam spillways into surface waters. Lead has been recognized as a contaminant in barite mill effluent since at least 1979 (USEPA 1979), and barite tailings discharged from the Star Mine tailings impoundment were found to contain 570 to 1,000 mg/kg lead (Integral 2014).

Barite tailings dam failures and decant water discharges are a recognized source of contamination to, and impairment of, the Big River. In 1975, tailings dam No. 4 failed at the Dresser Minerals Corporation mine/mill near Tiff, Missouri, on a tributary to Mill Creek. This failure resulted in the discharge of large quantities of tailings into Shibboleth Creek, which enters Mill Creek approximately 2.5 miles upstream from the Big River confluence. This tailings dam failure caused a fish kill extending 11.5 miles downstream and caused increased turbidity 70 miles downstream at the confluence of the Big River with the Meramec River (MDNR 2010b). The Missouri Department of Conservation has documented releases from two other Dresser Minerals operations in 1980 and 1982 that also produced fish kills in the Big River (MDC 2013). In addition, two tributaries of Mill Creek, Pond Creek, and Shibboleth Branch, are listed as impaired (i.e.., 303(d) listed) for inorganic sediments[5] and have total maximum daily loads (TMDLs) for cadmium, zinc, and lead, in addition to inorganic sediment (MDNR 2010a,b). Reports from the 1960s indicate that pools in Mill Creek were “choked with red clay from barite washing” (Kuester 1964, as cited by MDNR 2010b).

2.2.1.3 Hydrology of the SE Missouri Barite District

Mineral Fork and Mill Creek are the primary tributaries of the Big River that drain the SE Missouri Barite district. A graph of the gradients for these two creeks[6] (Figure 2-4) indicates that they have a similar gradient to the upper Big River (i.e., upstream of the SFCMA [around Irondale]). There exists very little hydrological data on the flow in either the Mill Creek or

[5] “Inorganic sediment is comprised of mineral particles, such as clay, silt, sand and assorted-sized rocks and other non-organic materials.” (MDNR 2012)

[6] Gradients were calculated using a digital elevation model and GIS.

Mineral Fork watersheds. Because of the paucity of measured data, an understanding of the hydrologic behavior of Mineral Fork was developed using the Big River as an analogous system.

Both stream gradient and the area of the Mineral Fork watershed (190 mi^2) are similar to those of the Big River watershed above the USGS gage at Irondale (175 mi^2; Table 2-3, Figure 2-4). Land use within both watersheds is dominated by woodland and grassland, with the upper Big River having somewhat more grassland in comparison to Mineral Fork (MDC 2012). Given the similarity of these watersheds, discharge data for Big River at Irondale was scaled by basin area to develop an estimate of discharge rates for Mineral Fork at the confluence with the Big River (Figure 2-5). This hydrograph indicates the following:

- Extensive periods of base flow—88 percent of the time discharge is less than 300 cfs (cubic feet per second; see histogram embedded in Figure 2-5)
- Limited periods of high storm flows, on the order of 1,000 to 6,000 cfs
- Very high storm flows (6,000 to 18,000 cfs) approximately once a year
- Rapid response to storm events (e.g., "flashiness").

The Mineral Fork hydrograph also provides an indication of the pattern of flows that would occur in Mill Creek and other smaller tributaries in the WCLD. This pattern of flows would suggest that sediment transport is dominated by infrequent periods of high flow, and that little sediment is moved during periods of base flow and low flow. However, during the high storm flows, significant sediment is likely to be eroded from the watershed and streambed and transported down Mill Creek and Mineral Fork to the Big River.

2.3 LEAD CONCENTRATIONS IN SEDIMENTS OF THE SE MISSOURI BARITE DISTRICT

Sediment samples have been collected from waterways in the SE Missouri Barite District on a number of occasions (Table 2-4) and have been analyzed for concentrations of lead and other metals. Lead concentrations ranged from non-detect to 4,040 mg/kg (Figure 2-6; includes data for all particle size fractions studied [<0.25 mm, <0.5 mm, and <2 mm]), with 26 samples (56 percent) greater than the preliminary effects concentration (PEC) of 128 mg/kg lead (MacDonald et al. 2000). The PEC is commonly used as a screening criterion for evaluating whether sediments contain metals concentrations at levels that may be of concern. These recent lead concentrations in sediment are likely considerably lower than lead concentrations that existed during the 270-year period of lead and barium mining in the SE Missouri Barite District. Given the hydrology and sediment transport potential of the creeks draining the SE Missouri Barite District, the sediments derived from this area will have contributed lead-bearing sediments to the Big River.

2.4 SURFACE MINING IN ST. FRANCOIS COUNTY

As occurred in Washington County, the earliest mining of lead in St. Francois County exploited surface and near-surface deposits of galena. This historical surface mining extracted massive crystals of galena that were found either in the residuum or occurred in crevices and caves in the uppermost portion of the bedrock. With the arrival of the diamond drill, many areas of historical surface mining were, subsequently, the locations of underground mining. Documented locations of historical surface mining are presented in Figure 1-3 and are based on early maps of surface mining and historical documents describing locations of surface mining (Schoolcraft 1819; American State Papers 1824, 1826; Swallow 1855; Buckley 1908; Dake 1930). The boundaries of the lead diggings should be considered both approximate and an underestimate of overall area because only the most significant diggings would have been documented. Additional evidence of the wide-scale existence of surficial mining in St. Francois County is provided by the fact that the U.S. government identified parcels of land that contained surficial lead ore, and in some cases reserved those parcels of land for the U.S. government (American State Papers 1826), and the history of Spanish and French land grants for lead mining prior to the Louisiana Purchase in 1803 (Schroeder 2002). Surficial lead mining in St. Francois County was conducted using the same methods used in the SE Missouri Barite District and yielded the same types of mining, milling, and smelting wastes. Total production of lead in St. Francois County during the surficial mining era was about 39,000 tons of lead (Table 2-2), which would have resulted in about 79,000 tons of lead lost to soils, sediments, and floodplain deposits in St. Francois County (Table 2-2).

2.5 ADDITIONAL MINING SOURCES OF LEAD TO THE BIG RIVER

In addition to the SFCMA and the SE Missouri Barite District, there are numerous other mining-related sources of lead to the Big River.

Two areas of intense mining activity within the Big River watershed were the Furnace Creek and the Valle Mines areas (Figure 2-2). EPA has defined the WCLD—Furnace Creek site as encompassing the southeastern corner of Washington County (USEPA 2012; Figure 1-1). However, the primary focus of mining activity in this area was on the northern side of the Big River in the Furnace Creek, Wallen Creek, and Hopewell Creek watersheds (Figure 2-2). Dake (1930) identifies this area as the location of lead diggings, and MDNR (2008) identifies numerous lead and barite mines in this area. The Valle Mines district straddles the Big River and the Joachim Creek watersheds, with about half of this mining district draining to the Big River by way of Bee Run (also called Bee Branch and Bee Creek in some references) and Tiff Creek (Figure 2-2). Mining at Valle Mines began in 1824, and by 1893 more than 8,500 tons of lead had been produced (Winslow 1894). In contrast to the Bonneterre dolomite-hosted deposits to the south, Valle Mines produced about twice as much zinc ore, 62,000 tons, as lead ore, 38,000 tons (Winslow 1894). Mining of lead and zinc ended in the 1920s, while barite mining continued through the 1940s.

There are numerous other creeks that drain lead and barite mining areas and discharge to the Big River in St. Francois, Washington, and Jefferson counties (Figure 2-2). A partial list of these creeks includes the following:

- Hazel Run, a tributary to Terre Bleue Creek, drains the Hazel Run diggings area (Schoolcraft 1819)
- Jim Coon Hollow, which drains the Dresser #6 barite mine, mill, and tailings pond
- Tiff Creek, which drains a portion of the Valle Mines district and also lead and barite mines in its lower reaches
- Maddin Creek, which drains the central portion of the SE Missouri Barite District
- Calico Creek, which drains the eastern side of the WCLD-Richwoods NPL Site.

Finally, there were lead mines and mills along the banks of the Big River that discharged directly to the river. A partial list of these included:

- Doggett's and Manchester diggings in St. Francois State Park.
- Frumet mine and mill, located on the east bank of the Big River, upstream of the confluence with Calico Creek (Figure 1-1). The Frumet operations produced up to 3 million lb of lead per year (lead mass based on 107 pigs of lead produced per day [Campbell 1875] at 80 lb lead per pig [Broadhead 1874])

Based on the above information it is clear that large masses of lead from the SE Missouri Barite, Furnace Creek, and Valle Mines districts have impacted the sediments and floodplains of the Big River. Smaller amounts of lead were also contributed by creeks draining individual mines and by lead diggings, mills, and smelters that discharged directly to the Big River. The denuded landscape and disturbed soils in these mined areas would have resulted in extensive erosion and produced lead-rich sediments that were transported to the Big River.

2.6 BACKGROUND LEAD

Because the Big River and its tributaries have been eroding the lead-bearing Bonneterre and Potosi dolomite formations and the overlying lead-bearing soils since the drainage basin was formed, the Big River sediments and floodplain deposits will be naturally high in lead. These background lead concentrations can be broken down into three general sources: 1) sediments entering the SFCMA from upstream, 2) erosion of the Bonneterre formation by the Big River and its tributaries, and 3) erosion of naturally mineralized soils. Each of these sources of lead is discussed below.

2.6.1 Upstream Sediments

The geometric mean lead concentration of Big River sediments upstream of the SFCMA is 33 mg/kg (range of non-detect to 2,357 mg/kg) (Table 2-5, Figure 2-6). Note that two of these samples (2080/65.5 with 2,357 mg/kg lead and BKG11 with 432 mg/kg lead, Table 2-5) contain lead concentrations considerably greater than the rest of the data set. Both of these samples were collected downstream of areas where early surficial mining had occurred and near land parcels identified by the U.S. government as having lead ore present. Thus, some sediment entering the SFCMA from upstream contains elevated lead concentrations that are due to mining activities not related to the SFCMA.

2.6.2 Erosion of the Bonneterre Formation

The St. Francois Mountains form the headwaters of the Big River watershed. The core of these mountains is Precambrian igneous rocks. During the Cambrian era (541 to 485 million years ago) this area was covered with seas, which deposited the sedimentary rocks that exist as the current bedrock formations. The sedimentary formations, in the order of deposition are: Lamotte sandstone, Bonneterre formation (almost entirely dolomite in the lead/zinc-mining region and predominantly limestone outside of this area), Davis shale, Derby-Doe Run dolomite, Potosi dolomite, Eminence dolomite, Gasconade dolomite, Roubidoux formation, and Jefferson City dolomite (Fluor Daniel 1995). Figure 2-7 presents a map of bedrock geology in the Big River watershed (USGS 1985) that shows both the extent of the Bonneterre formation and the areas where early surficial mining occurred.

The course of the Big River is determined by bedrock geology and faulting, as is evident from comparison of the river course with bedrock geology maps and fault zones. Because galena (with a hardness of 2.5 on the Mohs hardness scale of 1 to 10 [Hurlburt and Klein 1977]) is softer than the surrounding dolomite host rock of the SFCMA (with a hardness of 3.5–4.0), the Big River would have preferentially flowed through, and eroded, zones of galena mineralization. Erosion of mineralized zones within the Bonneterre dolomite produced sediments that are enriched in lead relative to the Big River sediments derived from non-mineralized Bonneterre dolomite or other formations. This pattern of high lead concentrations (600 to 2,000 mg/kg) in zones of mineralization, and low lead concentrations (<25 mg/kg) in non-mineralized zones was observed during sampling of Bonneterre surface outcrops (Integral 2014).

2.6.3 Erosion of Naturally Mineralized Soils

In addition to contributions of lead from direct erosion of the Bonneterre dolomite, background lead in Big River sediments and floodplain deposits is derived from erosion of naturally mineralized soils. These soils are divided into three categories, the naturally mineralized soils from throughout the Big River watershed, the soils within the Bonneterre-Davis contact zone, and the soils from areas that were surficially mined.

2.6.3.1 Soils from Throughout the Big River Watershed

Current Big River sediments and surficial flood plain deposits that are not of mill-related origin are derived from erosion of soils in the Big River watershed. There are five background soil data sets available for the Big River watershed (i.e., soils not impacted by operations at the SFCMA), which can be found in the following studies: the Doe Run background study (Integral 2014), the SFCMA ecological risk assessment (USEPA 2006), the Potosi ecological risk assessment (USEPA 2008), the Pluto soil survey (USGS 1998), and the 38th Parallel Transect Study (USGS 2005). These data sets are described in detail in Integral (2014) and the results of all five data sets are summarized on Figure 2-8.

Background soil lead concentrations in the Big River watershed are characterized by values that are generally less than 200 mg/kg, with a significant population that contain more than 400 mg/kg lead (46 out of 165 samples, or 28 percent). The data exhibit high variability, with individual samples having concentrations greater than 10,000 mg/kg lead. This pattern is consistent with observations of soil overlaying ore veins (Huff 1952), where areas in close proximity to lead outcrops have high concentrations, and concentrations decrease with distance from the outcrop. Spatially, this pattern leads to "islands" of high concentrations surrounded by areas of low concentrations. Random sampling of this pattern would lead to a data set with high variability in observed lead concentrations, a pattern that was observed in all five of the background data sets.

2.6.3.2 Soils from the Bonneterre-Davis Contact Zone

During the process of ore deposition, mineralizing fluids extended throughout the Bonneterre formation and deposited both disseminated galena dispersed within the Bonneterre formation and massive galena in cracks and fissures. Overlaying the Bonneterre is the less permeable Davis shale. When these mineralizing fluids encountered the less permeable shale, they were either stopped or were able to penetrate only a short distance (Sweeney et al. 1977). The result of this process was the deposition of galena at the contact between the Bonneterre and the Davis geological units. The Davis-Bonneterre contact (Figure 2-7) refers to a line tracing the location where the contact of the Davis shale and Bonneterre dolomite is at the bedrock surface. Because of variations in uplift and surface erosion, it traces a sinuous path through the Big River watershed. As solution weathering of the dolomite (largely a process of dissolution) exposed the bedrock around the Bonneterre-Davis contact, the lead from the galena deposits became concentrated in the residuum and surficial soils. Evidence of the importance of the Bonneterre-Davis contact in controlling surficial lead concentrations can be seen in the clustering of surficial mining areas along the contact (Figure 2-7). Based on the soil lead data collected in the residential areas of the SFCMA, a zone that extends about 600 m on either side of the contact line contains elevated lead concentrations (Integral 2014); this area is called the "Bonneterre-Davis contact zone." Background soil lead concentrations in the contact zone range from 7 to 16,300 mg/kg, with an average value of 821 mg/kg (Integral 2014)

2.6.3.3 Soils from the Surface Mined Areas

In contrast to the soils from throughout the Big River watershed and the soils from the Bonneterre-Davis contact zone, soils in the surface mined areas exhibit relatively consistent lead concentrations. For the surface mined soils, the dominant sample population ranges from 400 to 1,200 mg/kg lead, with relatively little variability (range of 72 to 1,700 mg/kg lead, and average of 783 mg/kg) (Integral 2014). This situation appears to have resulted from mixing of soils during historical surface mining, resulting in homogenization of the residual lead in the area of the diggings.

2.6.4 Estimation of Background Lead Concentrations in Sediment

A watershed model was prepared to evaluate the magnitude of lead inputs to the Big River from the erosion of lead-containing soils, such as naturally mineralized soils distributed throughout the watershed and soils impacted by historical surficial mining. A summary of the model is provided in Appendix A. Sediment loads were estimated using the Universal Soil Loss Equation, and subsequent assignment of lead concentrations to the modeled sediment loads allowed for estimation of lead mass entering the Big River. The model was applied to estimate lead loadings for two cases: present-day and historical surficial mining conditions. Present-day conditions are characterized by limited areas of disturbance, and provide an estimate of ongoing inputs to the Big River. Historical conditions are characterized by extensive areas of surficial mining and associated disturbance within the watershed, and provide an estimate of past inputs to the Big River. Disturbance due to surficial mining results in increased soil erosion from areas with elevated soil lead concentrations, greatly magnifying lead transport. The areas identified in Figure 1-3 (both the lead diggings as of 1824 and the surface mined areas identified by MDNR) were used as the area of disturbed lands due to surface mining. In-river sediment lead concentrations were calculated at a number of locations in the watershed (Figure 2-9.

Modeled current and historical sediment lead concentrations are fairly uniform along the Big River (Figure 2-10). This is due to the widespread distribution (and erosion) of naturally mineralized soils with elevated background lead concentrations. The SE Missouri Barite district is of particular importance because of elevated soil lead concentrations and, under the historical conditions, widespread surface disturbance (see Figure 1-3). The estimated sediment lead concentration is 320 mg/kg for present day conditions and 643 mg/kg under the historical scenario. Both of these sediment lead concentrations exceed the PEC of 128 mg/kg lead. This evaluation indicates that much of the observed sediment lead concentrations in the Big River could be derived from background watershed loadings alone.

2.7 RAILROAD BALLAST

Historical railways made use of readily available materials for construction of railroad beds; in the case of southeast Missouri, this material was primarily chat.

2.7.1 Operations and Ownership

The first railroad constructed within the SFCMA was the St. Joe & Desloge Railroad completed from Bonne Terre to Summit in Washington County in 1880 (NewFields 2007a). Subsequently, numerous rail lines were built in the vicinity of the SFCMA to haul ore, concentrate, and various chat, rock, and tailings products. The location of historical and current railroads is presented in Figure 1-2. Many of these rail lines eventually came to be owned by the Mississippi River and Bonne Terre Railway (MR&BT, formed in 1888). Through a series of mergers and acquisitions, the assets of the MR&BT were eventually acquired by the Union Pacific Railroad (Doe Run 2011).

2.7.2 Use of Chat in Railroad Beds

Historical railroads used large quantities of chat as railroad ballast and construction fill. These included locations, such as stream crossings, where it was necessary to construct ramps or where large quantities of fill were needed for grading (NewFields 2007a). In contrast, currently active rail lines must use ballast that meets American Engineering and Mining Association specifications, which chat does not. As a result, currently active rail lines do not use chat as a ballast component. In 2007, NewFields prepared an evaluation of the volume of chat and the concentration of lead in chat used as railroad ballast in the historical railroad beds in St. Francois County (NewFields 2007a). This analysis determined that there are approximately 1.3 myd^3 of chat, with a geometric mean lead concentration of 6,355 mg/kg, in the historical railroad beds of St. Francois County alone.

2.7.3 Releases to Surface Waters

NewFields (2007b) reports that chat has eroded from a MR&BT railroad crossing into Owl Creek just above the confluence of Owl Creek with the Big River (Figure 1-2). It was estimated that approximately 3,650 yd^3 of sediments (identified as either chat or a mixture of chat and cobble-sized sediments) are in Owl Creek or on its banks between the railroad crossing and the confluence with the Big River (NewFields 2007b). Based on the geometric mean concentration of lead in chat used for railroad ballast (6,355 mg/kg), this would correspond to approximately 40 metric tons of lead (assuming a chat density of 2.2 kg/L). NewFields (2007b) also reports that there is minor erosion of MR&BT railroad ballast into Turkey Creek, which flows north from Bonne Terre, but that the volume is too small to estimate.

3 QUANTITATIVE EVALUATION OF SOURCE AREA LEAD CONTRIBUTIONS

Analysis of sediment metals concentrations in the Big River identified lead, zinc, and barium as the key elements for defining signatures for different lead sources. These signatures identified three primary source areas in the Big River Watershed: the upper Big River, Flat River Creek, and the SE Missouri Barite District; however, signatures for lead contributions from smaller source areas, such as the Furnace Creek and Valle Mines areas, are also evident. A lead-zinc mixing model was used to identify the relative contributions of lead from the upper Big River and Flat River Creek, and a lead-barium mixing model was used to identify the relative contributions of lead from the SE Missouri Barite District and the SFCMA.

3.1 METAL CONCENTRATION PATTERNS IN RIVER SYSTEMS

In mining-impacted river systems, sediment metal concentrations decrease exponentially with distance from a source (USGS 1963; Helgen and Moore 1996; Miller and Orbock Miller 2007; Pavlowsky et al. 2010). This decrease is the result of the interaction of several processes:

- Mixing and dilution of the mining-related metals with tributary sediment inputs
- Selective deposition of the higher density minerals (e.g., metal sulfides) close to the source
- Deposition and dispersion of contaminated sediments in channel bars and overbank deposits.

Despite the fact that sediment metal concentrations tend to have considerable variability, this decrease in concentration with distance from the source has been consistently observed for river systems (Pavlowsky et al. 2010). Metal contributions from additional sources result in the overlay of multiple decay curves. Such curves can be mathematically deconstructed and used to establish the magnitude of the different metals sources.

3.2 METAL CONCENTRATION DATA ANALYSIS

Numerous studies have focused on characterizing metals concentrations in the soils, sediments, and overbank deposits of the Big River and, to a lesser degree, its tributaries. The studies relied on for the metals concentration data used in this analysis were Pavlowsky et al. (2010), Allert et al. (2010), Roberts et al. (2009), MDNR (2003, 2007, 2009, 2010b), and USEPA (2006, 2008); these data are presented in Table 3-1. For the Big River watershed, the combination of lead, zinc, and barium data provides differentiation between the primary source areas. These metals have low water solubility and are associated with, and transported along with, bulk sediment. These characteristics tend to preserve source signatures in sediments downstream from metals sources.

The data were pre-processed to facilitate data analysis and presentation. The confluence of the Big River and the Meramec was assigned a river mile (RM) of 0, and RM designations were assigned to each sediment sample in 0.1-mile increments. The data were then grouped by subdividing the river into 5-mile reaches (i.e., 0 to 5, 5 to 10, etc.); and all of the data for each metal located within each reach were averaged. This averaging provides an estimate of the central tendency of the concentration within each reach, and reduces the influence of individual extreme values. Reaches were truncated at Flat River Creek, Mill Creek, and Mineral Fork to ensure that the signatures of these major tributaries were not masked by averaging.

3.2.1 Lead and Zinc Sources and Concentration Patterns

Upstream of the SFCMA, lead concentrations in sediment are elevated above regional background due to contributions from historical mining at the Furnace Creek NPL site (drained by Furnace Creek, Wallen Creek, and Hopewell Creek) (Figures 2-2 and 3-1). The highest lead concentrations in Big River sediments are associated with the SFCMA between Hayden Creek (RM 112) and Terre Bleue Creek (RM 92) (Figure 3-1). This is followed by an exponential decrease in lead concentrations through RM 85. This uninterrupted decrease indicates that the mines at Bonne Terre, which were drained by Turkey Creek (confluence with the Big River at RM 87), did not make significant contributions of lead to Big River sediments. At RM 80, a “shoulder” appears in the curve, indicating the superimposition of a secondary decay curve. This shoulder is coincident with the confluence with Bee Fork, a tributary draining the Valle Mines area. Downstream of RM 70, lead concentrations remain elevated, with multiple additional peaks in the lead concentration profile, due to contributions of lead from the creeks draining the SE Missouri Barite District (Jim Coon Hollow, Mill Creek, Maddin Creek, Mineral Fork, Calico Creek, and Ditch Creek) and locations where mining, milling, and smelting occurred along the Big River, such as the Frumet mine and mill. Additional, smaller, lead sources also appear in the lead concentration profile in Jefferson County around Cedar Hill and Byrnes Mill (Figure 3-1).

The pattern of zinc concentrations in Big River sediments closely matches that of lead through the SFCMA (Figure 3-1). This is followed by a rapid decay in concentrations, and the shoulder in the curve associated with Bee Fork is consistent with contributions from the Valle Mines operations. In contrast to lead, downstream of Bee Run there is an asymptotic decrease in sediment zinc concentrations, approaching a baseline of less than 100 mg/kg. Zinc was not mined in the SE Missouri Barite District and concentrations in soils and sediments there are far lower than those in the SFCMA (USGS 1998, 2001).

Concentration patterns of lead and zinc in surface soils (0 to 12 in.) of the Big River floodplain are consistent with those in sediments, and demonstrate that the same sources that are contributing to sediment lead concentrations are contributing to floodplain soil lead concentrations (Figure 3-2). Based on the lead concentration profile, the Valle Mines area and the SE Missouri Barite District are the dominant lead sources to floodplain soils.

3.2.2 Barium Sources and Concentration Patterns

As with lead, barium concentrations in sediments are elevated upstream of the SFCMA due to contributions from the Furnace Creek mining area (Figure 3-1). Barium concentrations decrease downstream of the SFCMA and then increase dramatically as the Big River passes through the SE Missouri Barite District. The same barium concentration pattern is observed for surficial floodplain soils (Figure 3-2). These results confirm the large contributions of barium and lead originating from the SE Missouri Barite District.

3.2.3 Big River Floodplain Cores

On September 9 and 10 of 2013, AMEC Environment & Infrastructure, Inc. collected floodplain cores at both St. Francois State Park and Washington State Park. Cores were collected to a maximum depth of 20 ft or until outwash gravels were encountered. Screening-level metals concentration data for barium, lead, and zinc were collected using a hand-held x-ray fluorescence instrument (InnovX-Olympus DS-2000) in the field, and the resultant data were used to select samples for laboratory analysis. Soil samples were collected from across 1-ft intervals of each core and shipped to ALS Laboratories for analysis of barium, lead, and zinc by digestion (EPA Method 3050B) and analysis by inductively-coupled plasma/mass spectroscopy (EPA Method 6010B). The resultant data, including coordinates for each coring location are presented on Figure 3-3.

Results from cores collected in St. Francois State Park (SF-SB1 [high floodplain] and SF-SB3 [low floodplain]) have barium concentrations ranging from 60 to 250 mg/kg and maximum lead concentrations in the range of 4,000 to 7,000 mg/kg (Figure 3-3). However, the lead concentration in SF-SB1 peaks at about 4 ft below ground surface, while the lead in SF-SB3 peaks at 13–18 ft below ground surface. This suggests that lead at depth in core SF-SB3 is derived from either naturally mineralized material or early surficial mining (e.g., background for the SFCMA site) because if this lead were derived from the hard rock mining era, it would occur near the top of the core.

Metals composition in the cores from Washington State Park are distinctly different from those collected at St. Francois State Park and contain barium concentrations that are approximately equal to lead concentrations (Figure 3-3). The maximum barium concentrations in the Washington State Park cores are nearly 10 times those in the St. Francois State Park cores. These results indicate that barium, and associated lead, from the SE Missouri Barite District are the dominant source of metals to floodplain materials in Washington State Park. It should be noted that these cores were collected upstream of Mineral Fork (Figure 1-1), which is the largest Big

River tributary draining the SE Missouri Barite District. As a result, lead contributions from the SE Missouri Barite District to the Big River will increase downstream of Washington State Park.

3.3 END-MEMBER MIXING MODELS

There are a number of mathematical techniques that can be used to apportion contributions of metals from specific sources when those sources contain either unique metals, or unique combinations of metals. For this analysis, end-member mixing analyses were applied, which is a common technique for apportioning contributions of metals to sediments in river systems (e.g., Marcus 1989; Helgen et al. 2007; Bird et al. 2010).

3.3.1 Lead/Zinc Mixing Model

For the upper portion of the Big River watershed, through RM 80, a lead-zinc mixing model was used to allocate between lead originating from the upper Big River and Flat River Creek. This is possible because sediments in the upper Big River have a lower a lead-to-zinc ratio (0.9) than sediments in Flat River Creek (28.1). A two-component mixing model was used to calculate the percent contribution of lead from each of the two sources. Below the confluence of the Big River and Flat River Creek, the source contribution of the upper Big River (50 to 60 percent) is nearly equal to that of Flat River Creek (40 to 50 percent) (Figure 3-4). At RM 80, Bee Run contributes sediment with a low lead-to-zinc ratio. This results in an apparent increase in upper Big River contributions. This observation demonstrates the utility of an end-member mixing model for identifying lead contributions in situations where multiple inputs of lead are present. Farther downstream, the river is influenced by multiple additional lead and zinc sources, and the model results cease to be illustrative of specific lead source contributions.

3.3.2 Lead/Barium Mixing Model

Because of the barium concentrations emanating from the SE Missouri Barite District, lead-to-barium concentration ratios can be used to differentiate between lead coming from the SE Missouri Barite District versus the SFCMA. Samples of sediments and soils found within the SFCMA have much higher lead-to-barium ratios than those from the SE Missouri Barite District (Figure 3-5). Samples from the SE Missouri Barite District have a relatively broad range of lead-to-barium ratios, but the ratio is generally less than 1 (more barium than lead). In contrast, lead-to-barium ratios in soil and sediment of the SFCMA are much greater than 1. This difference provides an ideal situation for the application of a lead/barium mixing model to allocate contributions of lead from the SFCMA versus the SE Missouri Barite District.

Upstream of the SFCMA, there appears to be a small contribution of lead from the SE Missouri Barite District (Figure 3-6); the calculated contribution appears to be due to a combination of sample variability and contributions of lead from the Furnace Creek Area. Between RM 90, at the downstream end of the SFCMA, and the Meramec River, the SE Missouri Barite District becomes the dominant source of lead to Big River sediments (Figure 3-6). These results should be considered semi-quantitative, as evidenced by the variability in the model results, which is due to high variability of lead and barium concentrations in both the SE Missouri Barite District and in sediments of the Big River. Nonetheless, the results demonstrate that sediments in the lower Big River have a signature consistent with that of the SE Missouri Barite District.

4 SEMI-QUANTITATIVE ALLOCATION OF LEAD CONTRIBUTIONS TO THE BIG RIVER WATERSHED

This semi-quantitative allocation of lead contributions to the sediments of the Big River is based on the historical research, trends in sediment metals concentrations, and results from the watershed and mixing models. This allocation is presented as proceeding from upstream of the SFCMA, down the length of the Big River, to its confluence with the Meramec River (Figure 4-1). This figure presents a best estimate of the contributions from each lead source as stacked bars, where each bar sums to 100 percent and is associated with the y-axis on the left side of the plot. The average lead concentration in Big River sediments (data collected between 2003 and 2010) is also presented, and is associated with the right side y-axis. Numerical values for these estimates are presented in Table 4-1.

Big River sediment lead concentrations increase from an average background value of 38 mg/kg upstream of all mining inputs to around 130 mg/kg as lead from the Furnace Creek mining district enters the Big River (Figures 2-2 and 4-1). As a result, sediment lead concentrations exceed the PEC of 128 mg/kg upstream of the SFCMA. As the Big River enters the SFCMA, erosion of mineralized soils, under current conditions, becomes a significant source of lead to sediments, equivalent to approximately 320 mg/kg lead. During the surficial lead mining era the contribution of lead from soil erosion would have been considerably greater (estimated to be approximately 640 mg/kg based on the results from the watershed model), due to the large areas of denuded and disturbed land around the lead diggings. From Eaton Branch, which drains the mining operations at Leadwood, to the confluence with Flat River Creek, lead concentrations increase substantially due to inputs from the upper Big River mining sources. Downstream of the confluence of the Big River and Flat River Creek (RM 99) lead concentrations continue to increase due to contributions from mining sources along Flat River Creek. The lead/zinc mixing model indicates that lead source contributions are about evenly split between the upper Big River and Flat River Creek. Mill Creek marks the beginning of significant inputs from the SE Missouri Barite District. Downstream of this point, the lead/barium mixing model indicates that contributions of lead from the SE Missouri Barite District dominate lead contributions to the Big River. In the last 40 miles above the confluence with the Meramec River, contributions from the SE Missouri Barite District decrease and background lead from erosion of mineralized soils becomes the dominant lead source to Big River sediments.

5 CONCLUSIONS

To establish the magnitude of different lead sources to sediments and floodplain deposits of the Big River, a variety of techniques were investigated, including metal concentration profiles, metal ratios, mixing models, and results from a watershed model. Results from these analyses, in combination with documentation of historical mining practices, indicate the following:

- The Furnace Creek mining area is contributing lead and barium to sediments upstream of the SFCMA.
- Background lead from erosion of naturally mineralized soils contributes about 320 mg/kg lead under current conditions (background sediment lead concentrations were about twice this amount during the surficial mining period).
- Mining operations on Flat River Creek and the upper Big River contributed about equally to lead concentrations in sediments downstream of their confluence.
- The mining operations at Bonne Terre did not make significant contributions of lead to Big River sediments or floodplain deposits.
- The SE Missouri Barite District is the primary source of lead to Big River sediments and floodplain deposits of the lower Big River.

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FIGURES

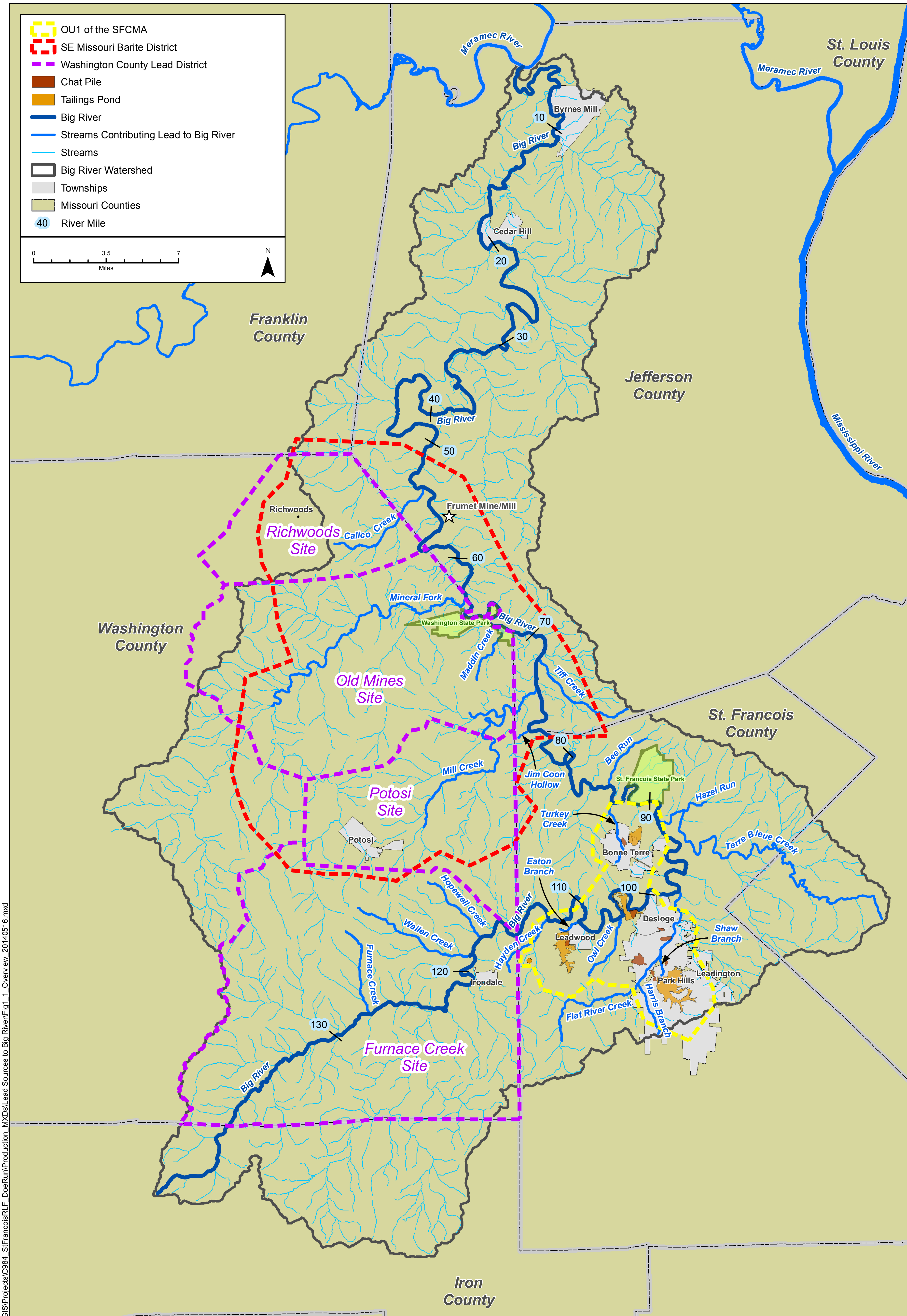

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Figure 1-1.
Big River Watershed Overview

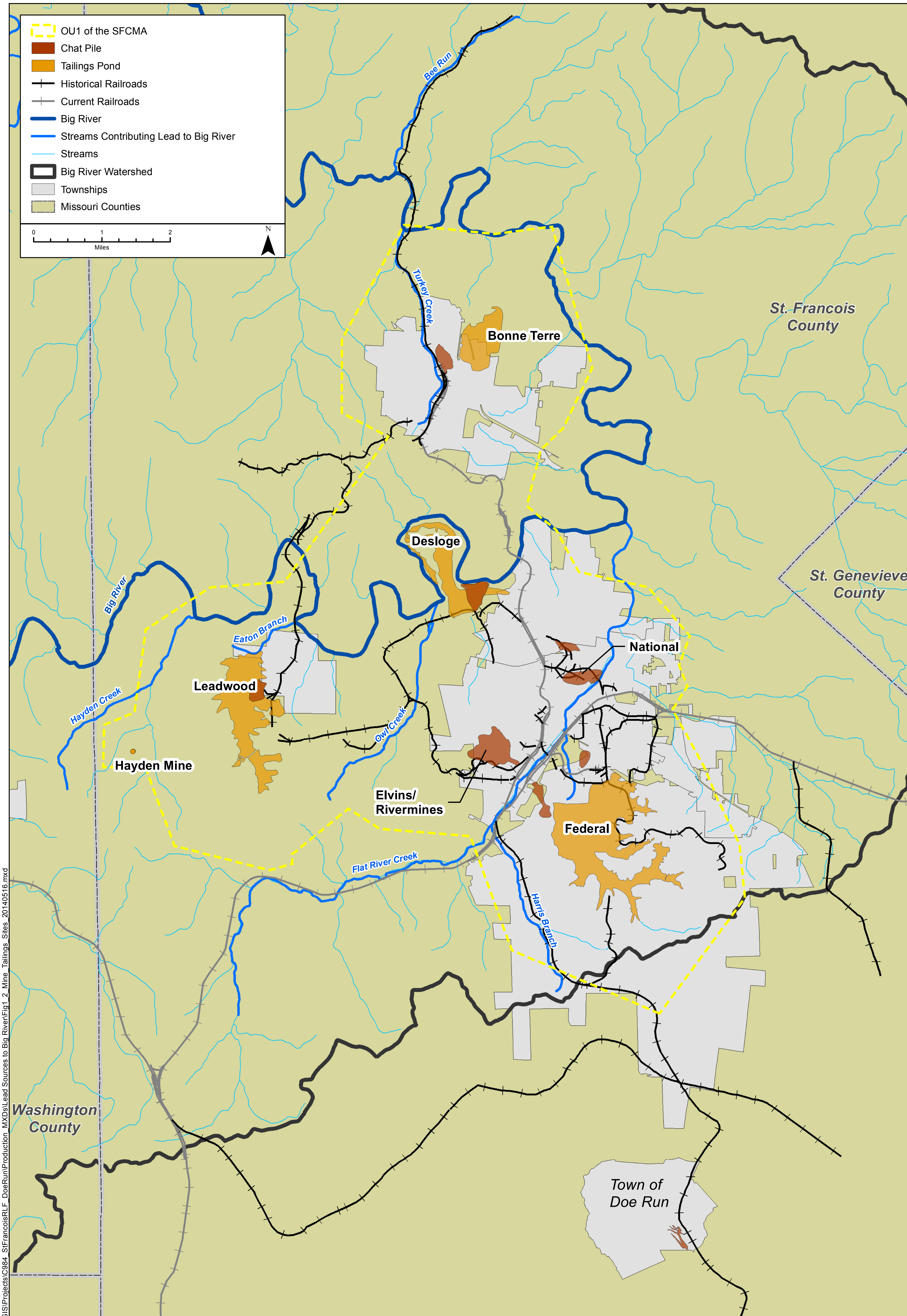

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Figure 1-2.
Location of Historical and Current Railroads at the St. Francois County Mining Area

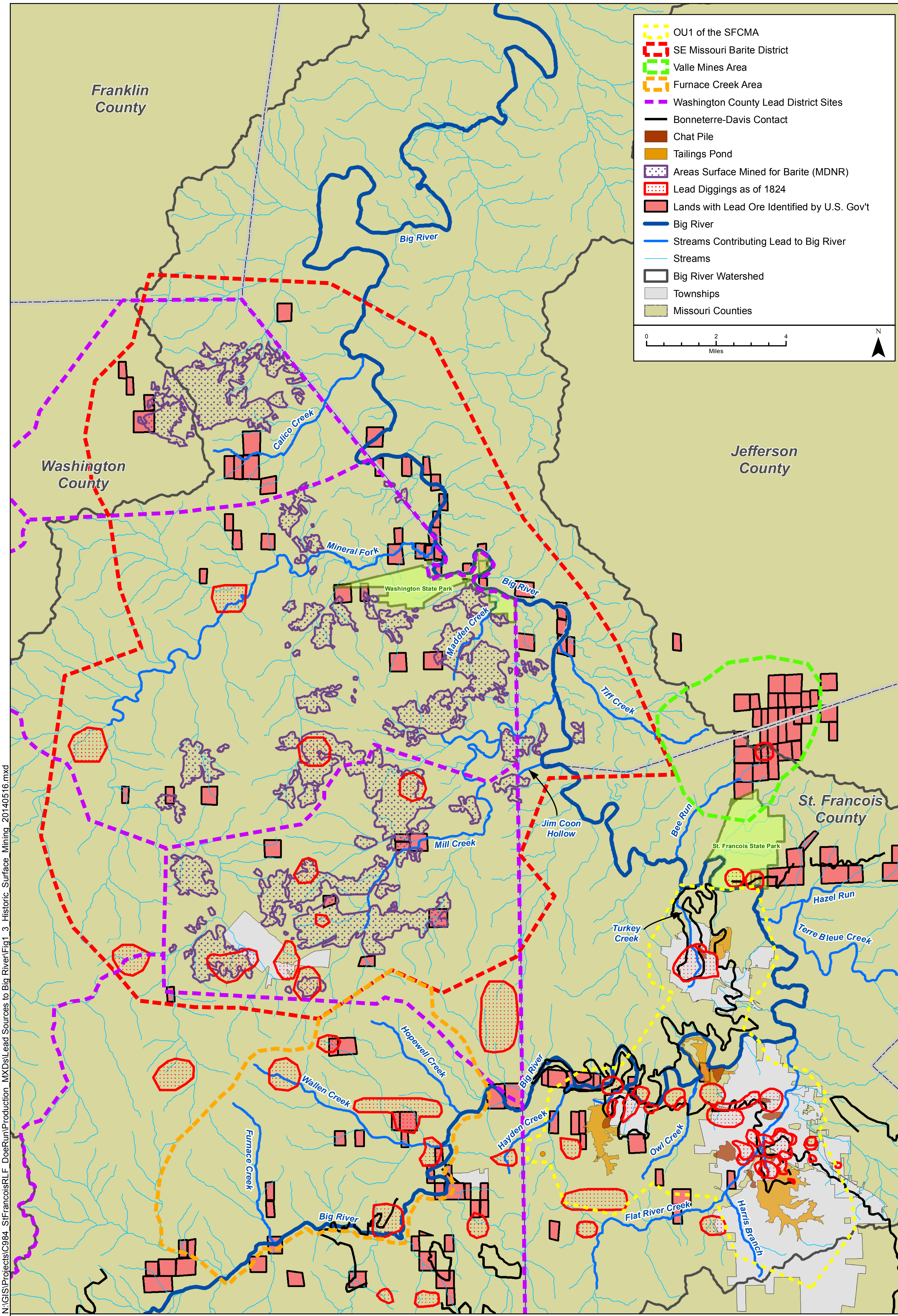

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Figure 1-3.
Historical Surface Mining Areas in the Big River Watershed

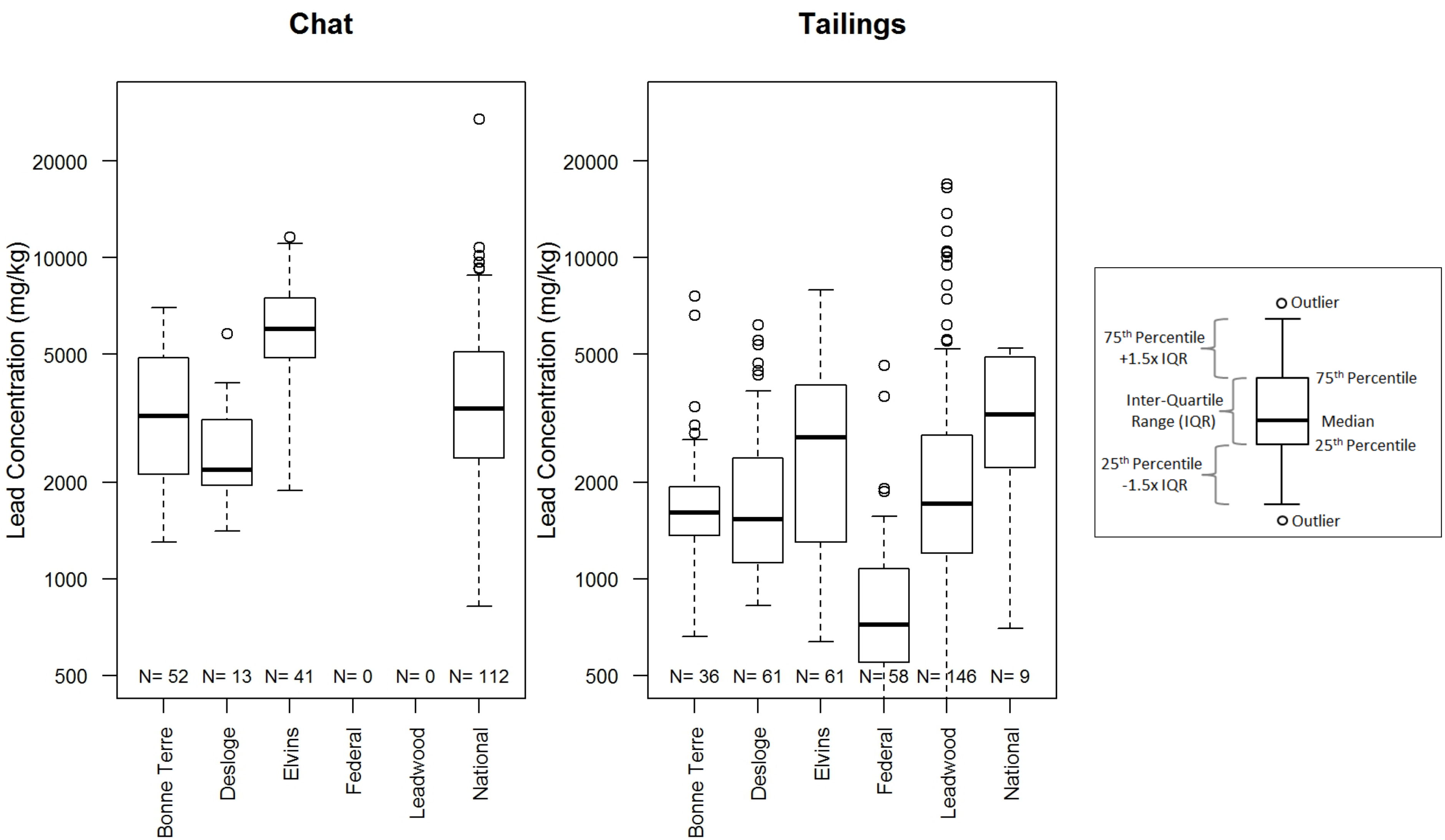

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Figure 2-1.
Concentrations of Lead in Chat and Tailings

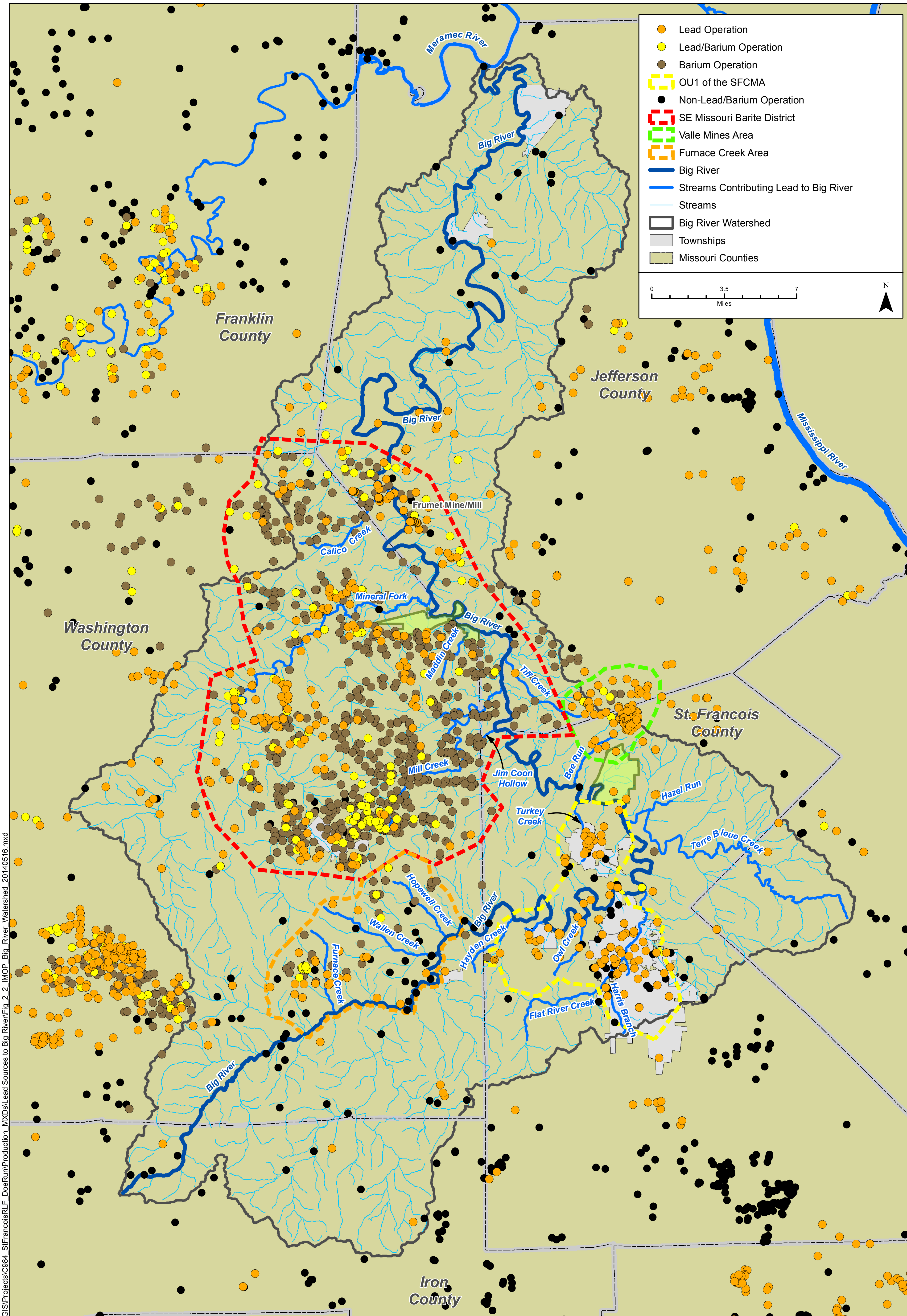

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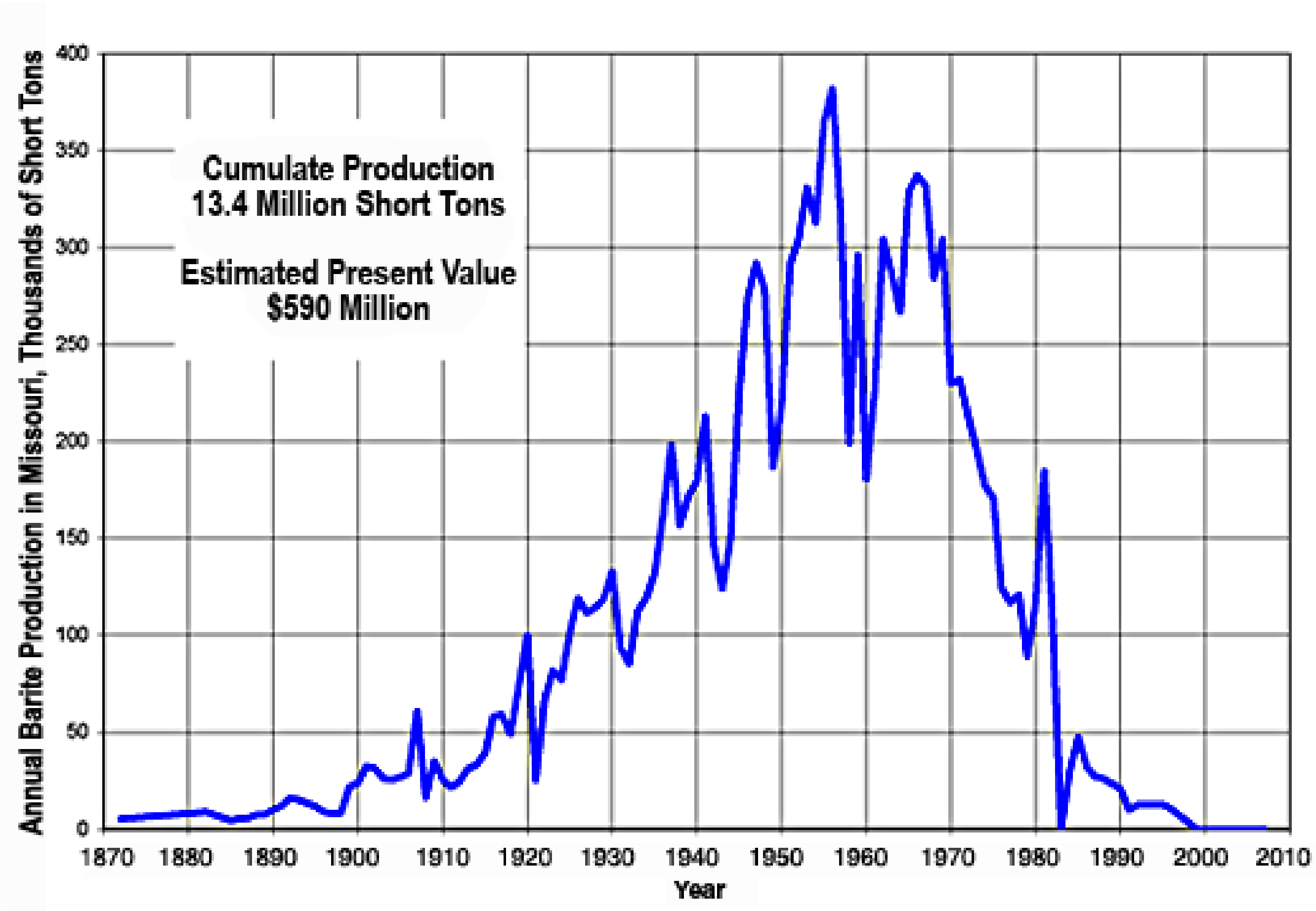
Figure 2-2.
Density of Mining in the Big River Watershed



Source: http://www.dnr.mo.gov/geology/geosrv/imac/barite.htm

Figure 2-3.
Production of Barite in the State of Missouri

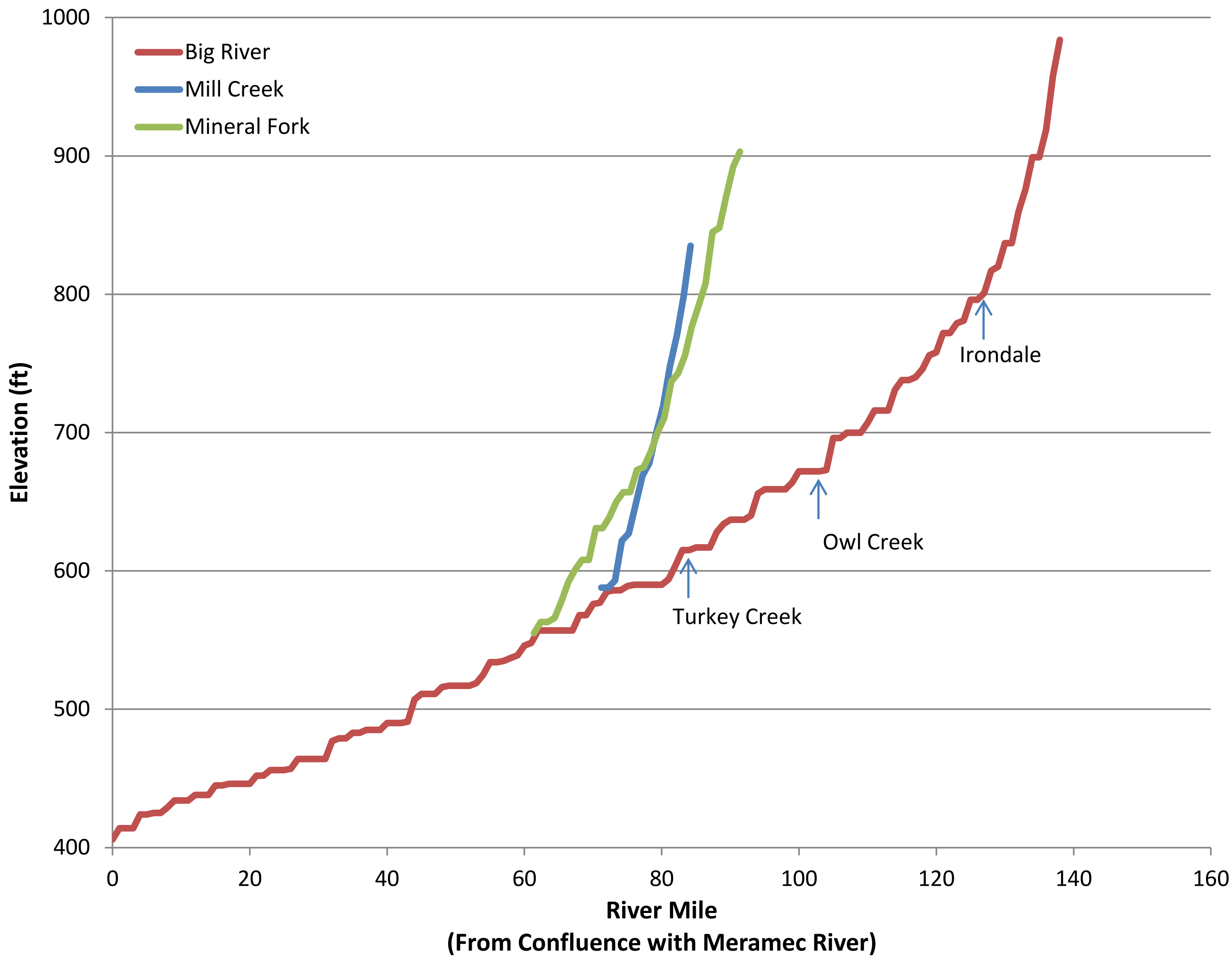


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Figure 2-4.
Stream Gradients for Big River, Mill Creek, and Mineral Fork

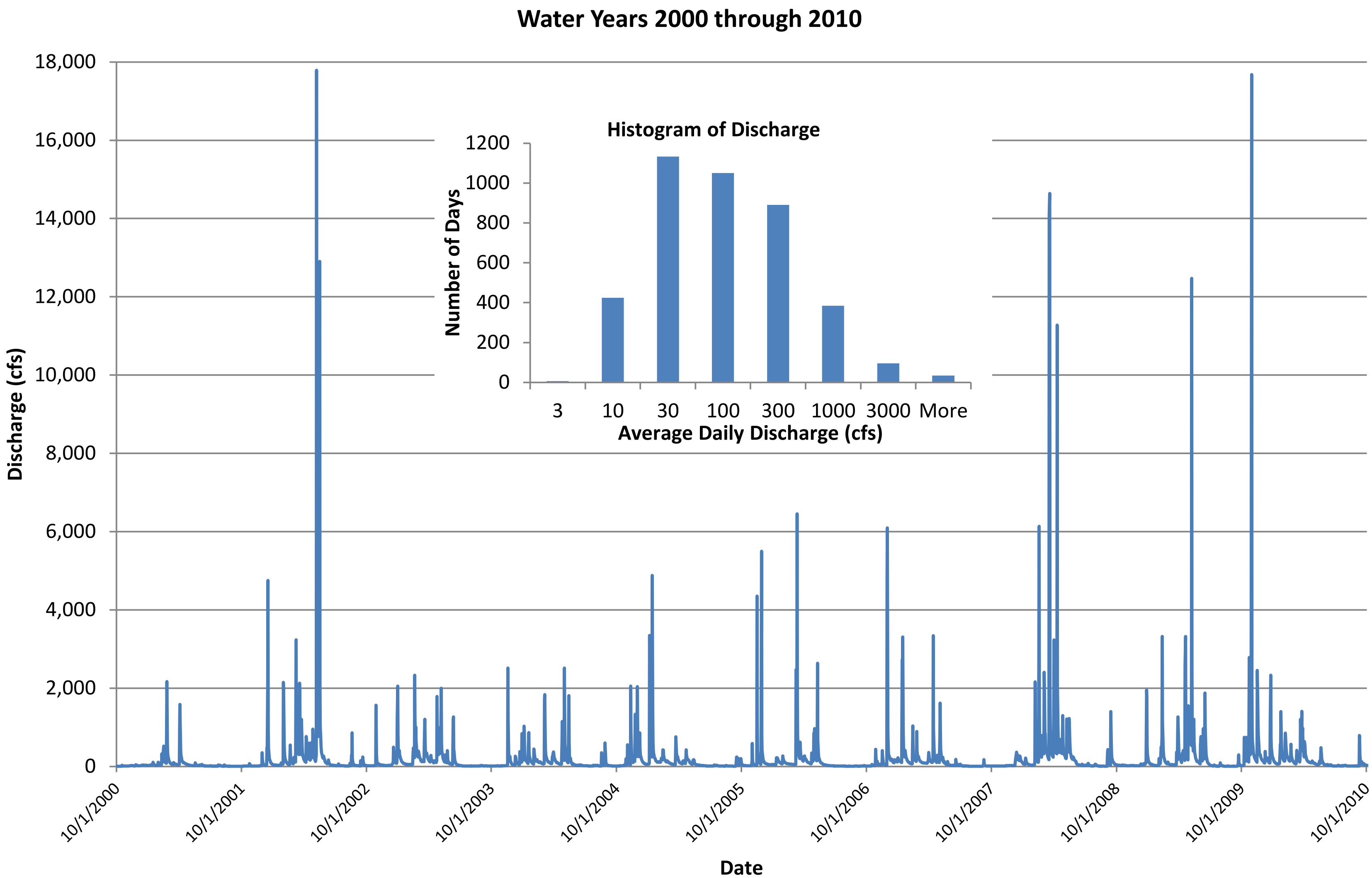

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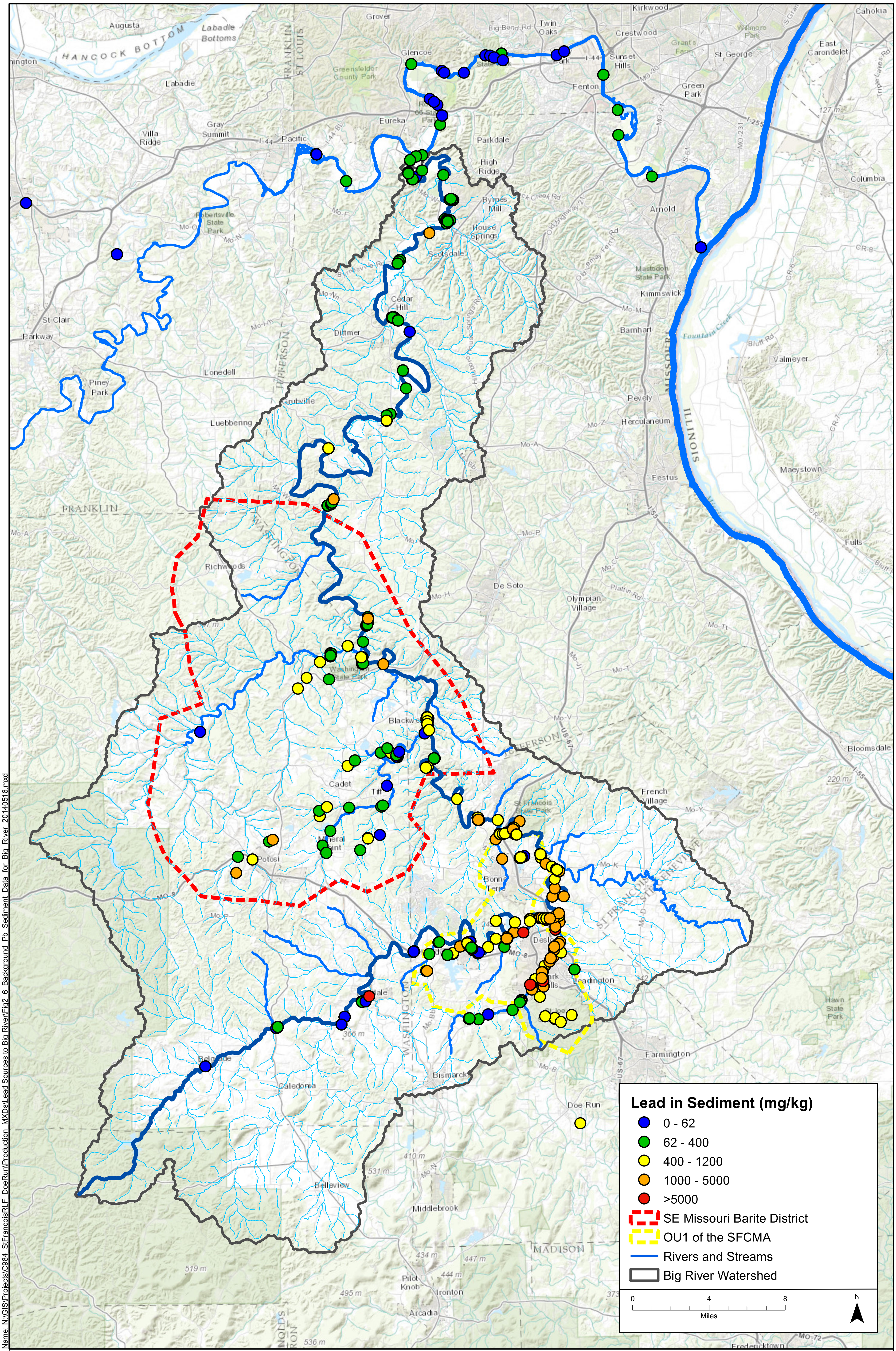
Figure 2-5.
Hydrograph of Estimated Mineral Fork Discharge at Confluence with the Big River



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SOURCE: Background Image; Sources: Esri, HERE, DeLorme, TomTom, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), swisstopo, MapmyIndia, © OpenStreetMap contributors, and the GIS User Community

Figure 2-6.
Lead Concentrations in Sediments of the Big River Watershed

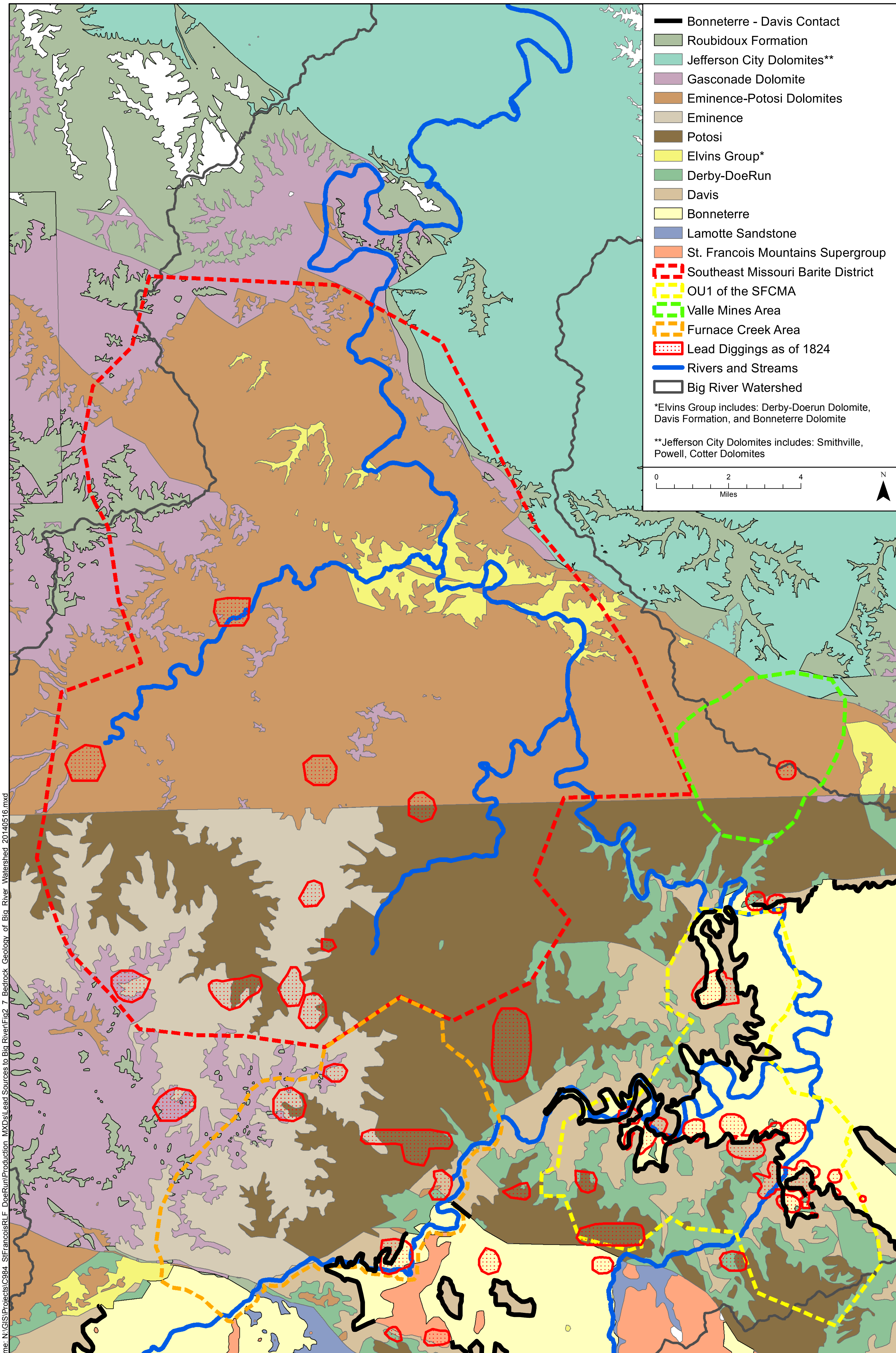

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Figure 2-7.
Bedrock Geology of the Big River Watershed

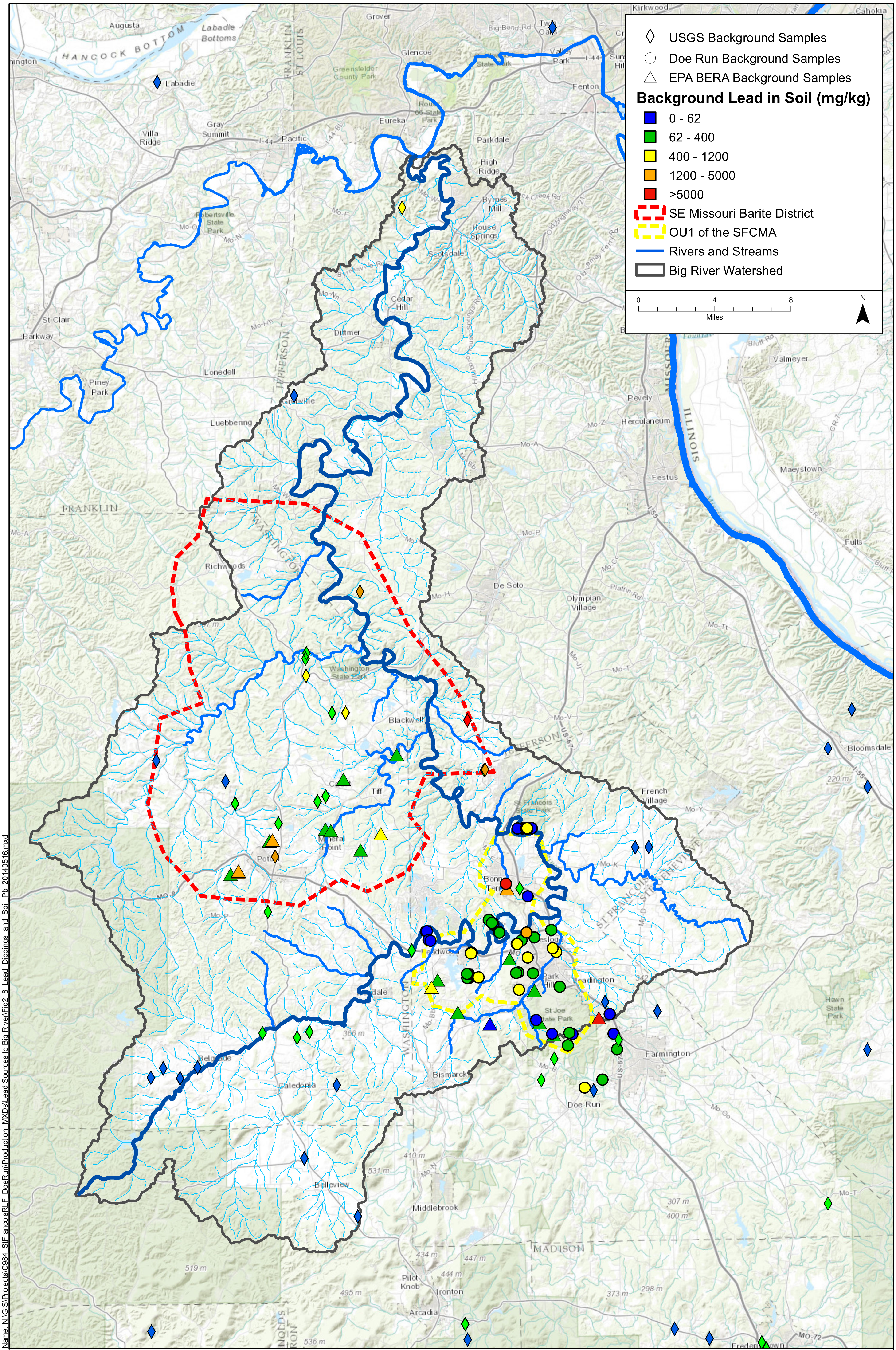

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Figure 2-8.
Background Soil Lead Data in the Big River Watershed

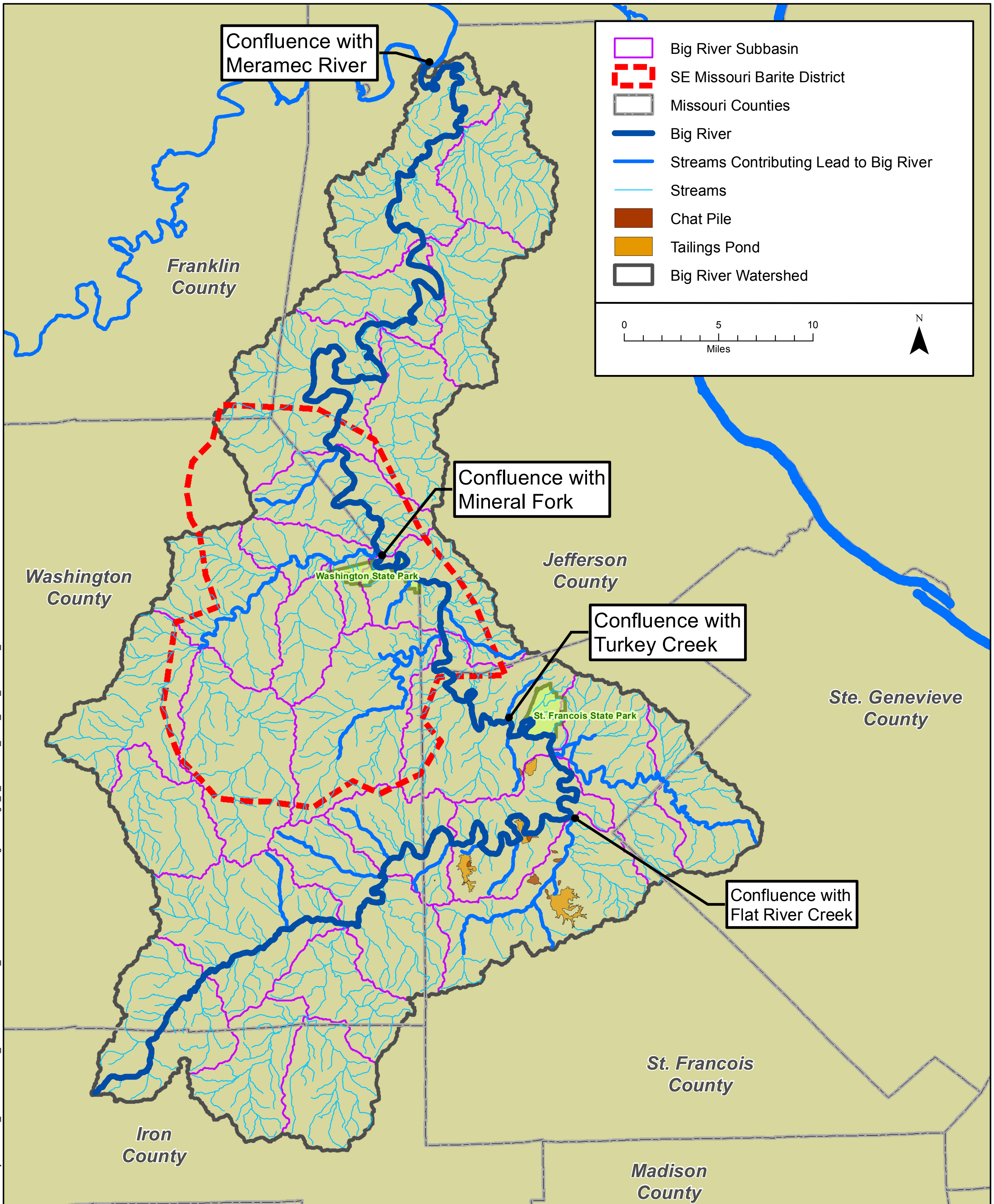

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Figure 2-9.
Sediment Load Calculation Locations
for the Watershed Model

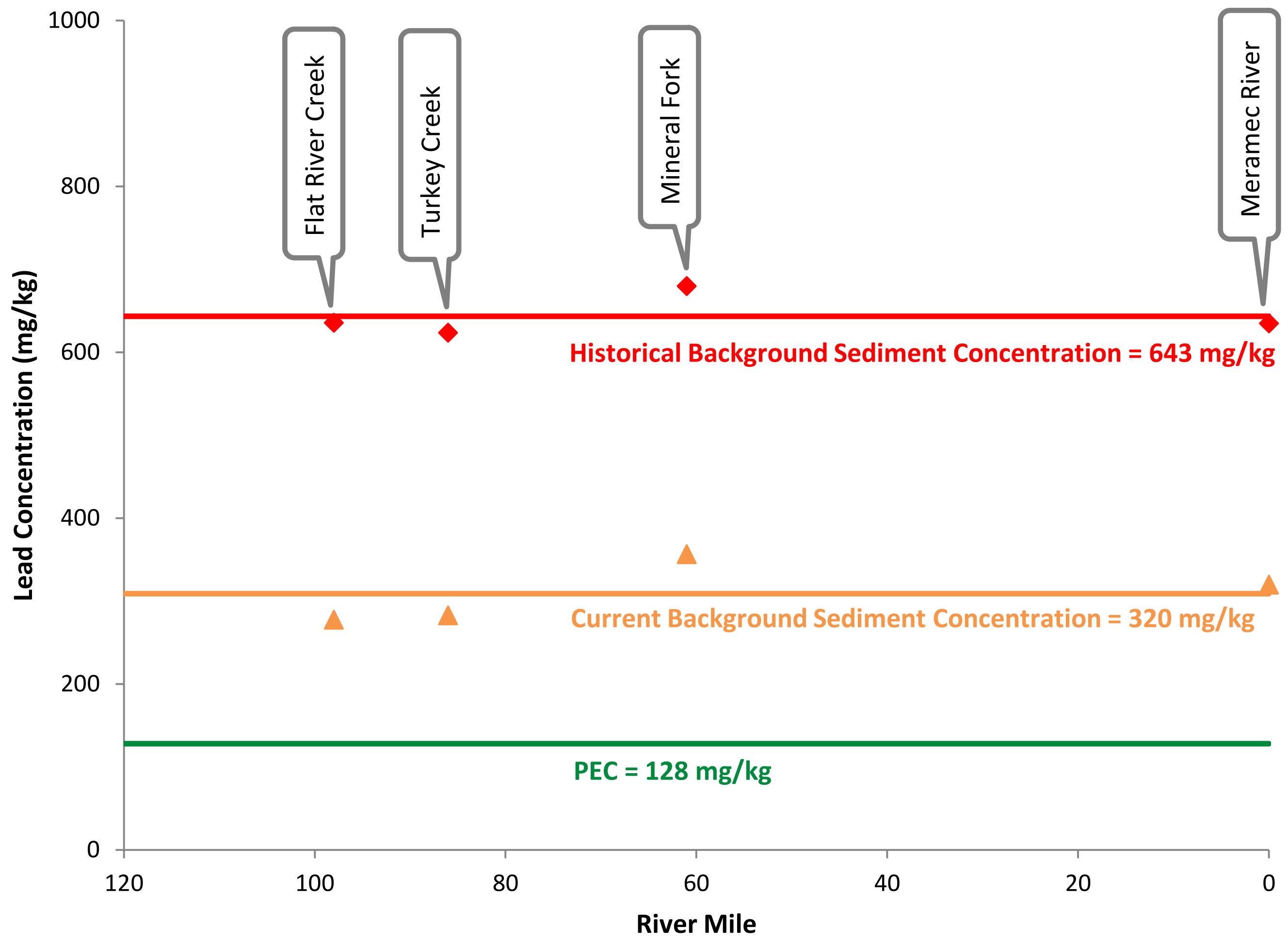

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Figure 2-10.
Estimated Sediment Lead Concentrations in the Big River

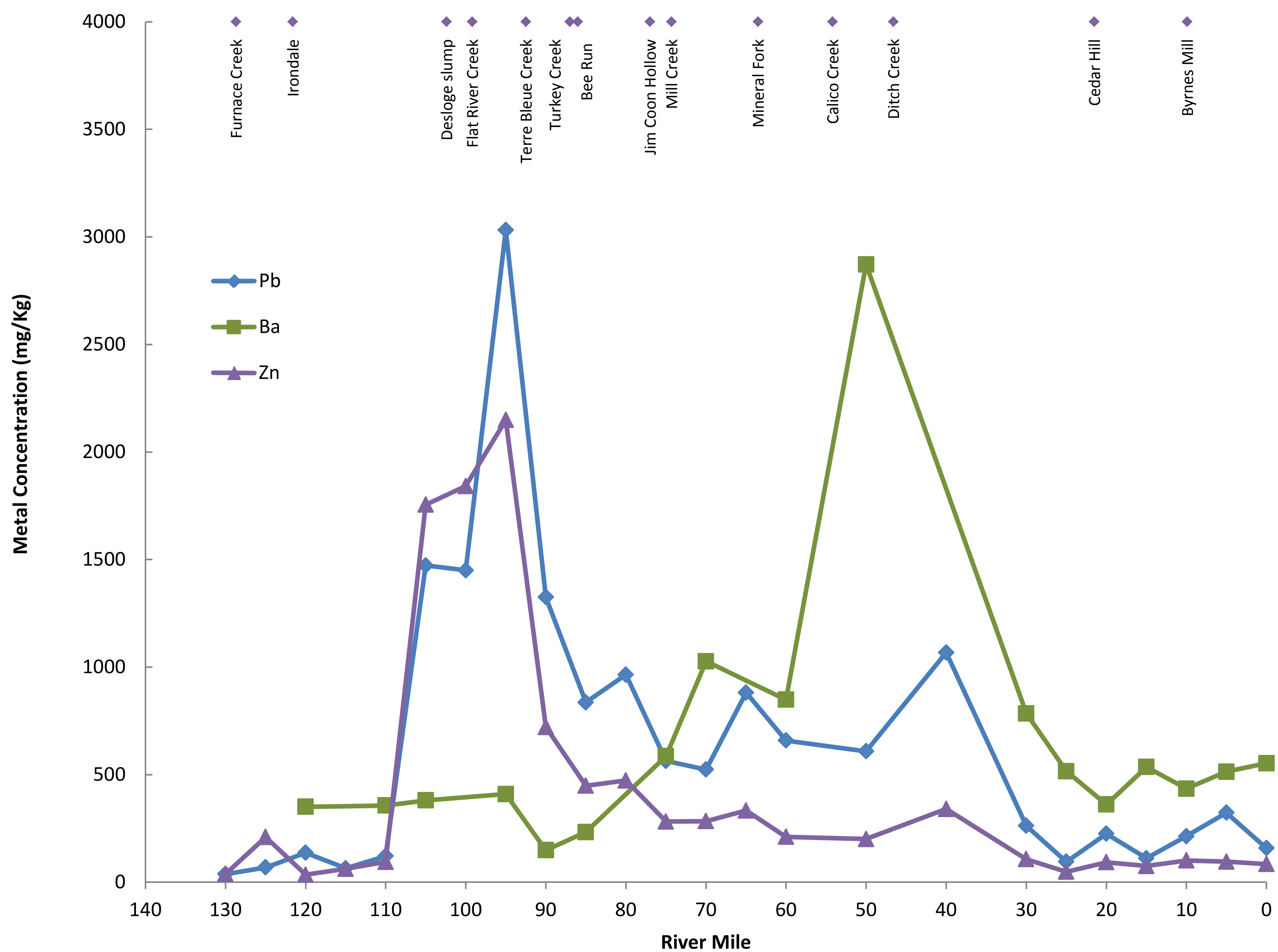

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Figure 3-1.
Sediment Metals Concentrations in the Big River, Averaged over 5-Mile Reaches

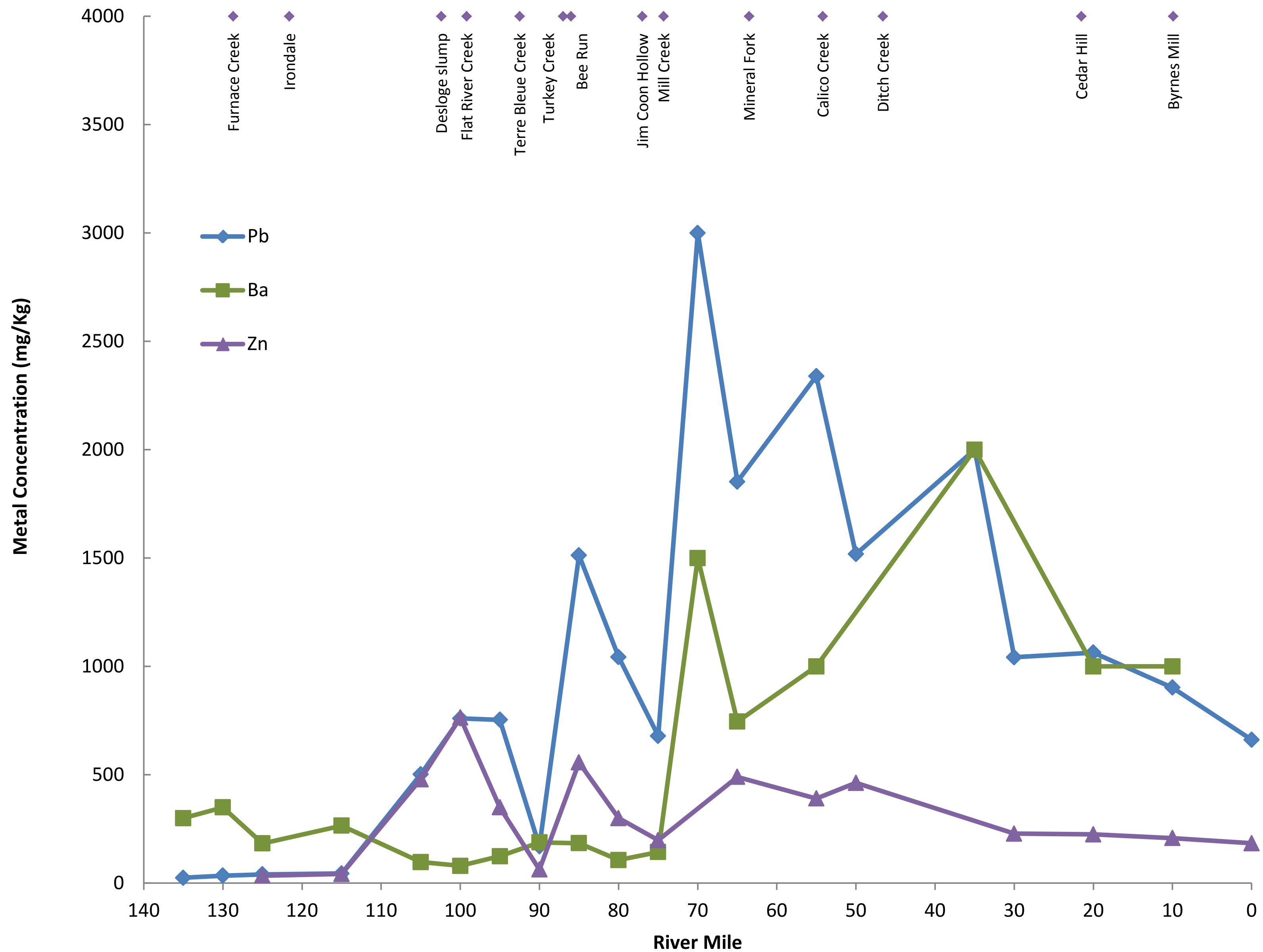

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Figure 3-2.
Floodplain Soil Metals Concentrations in the Big River, Averaged over 5-Mile Reaches (Surface Only)

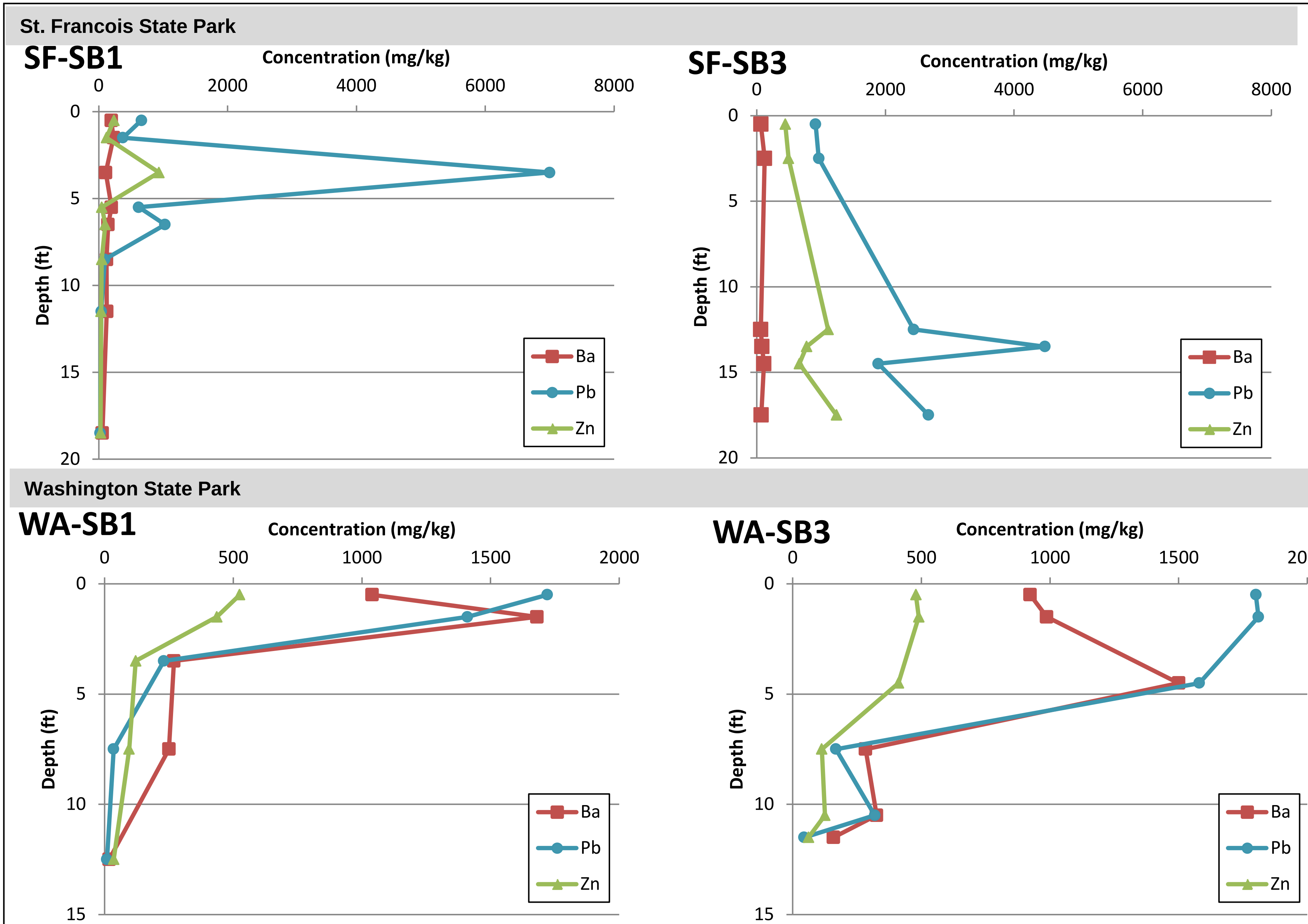

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Figure 3-3.
Floodplain Core Results from St. Francois State Park and Washington State Park

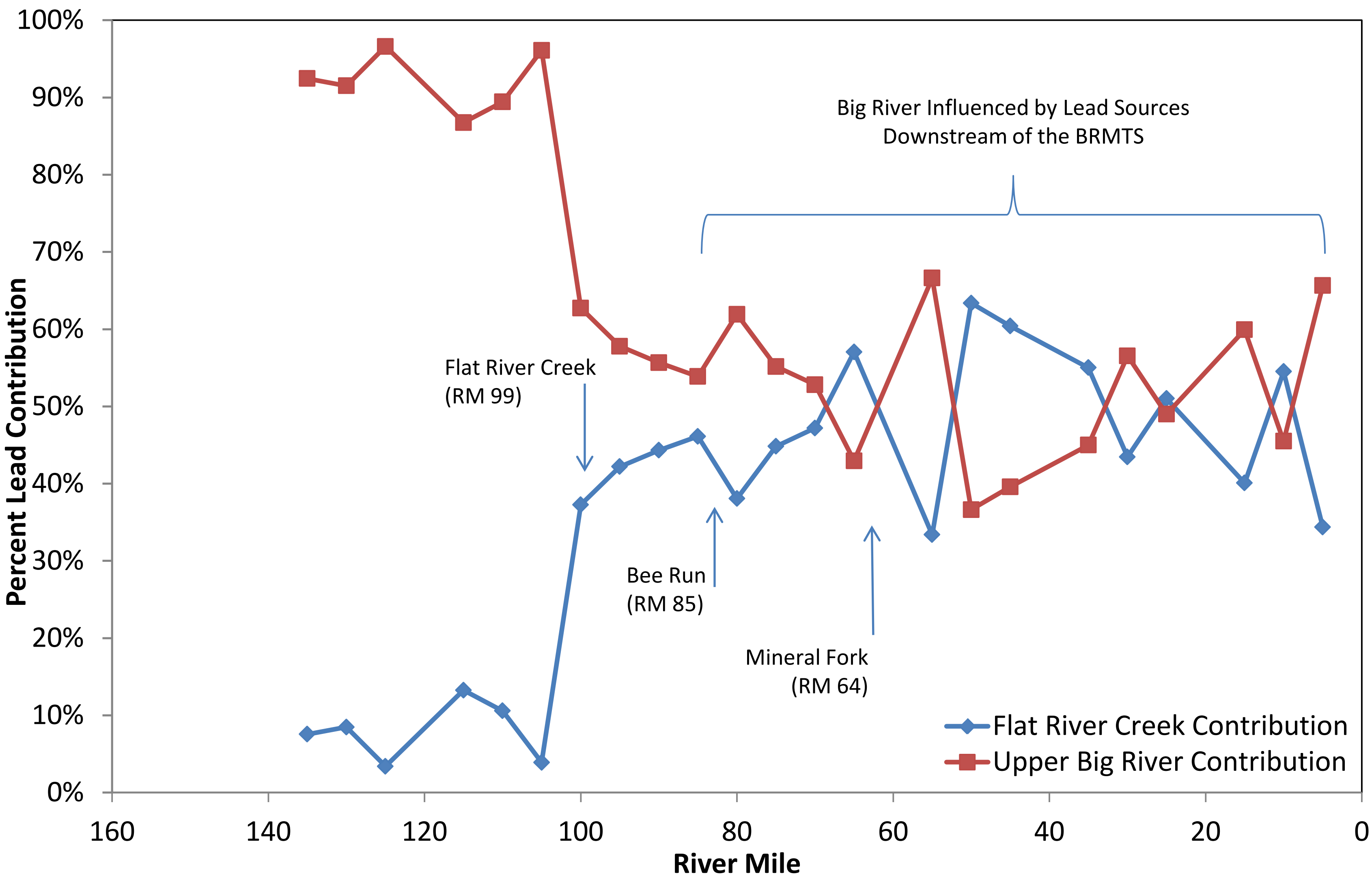

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Figure 3-4.
Lead-Zinc Mixing Model Results for the Big River

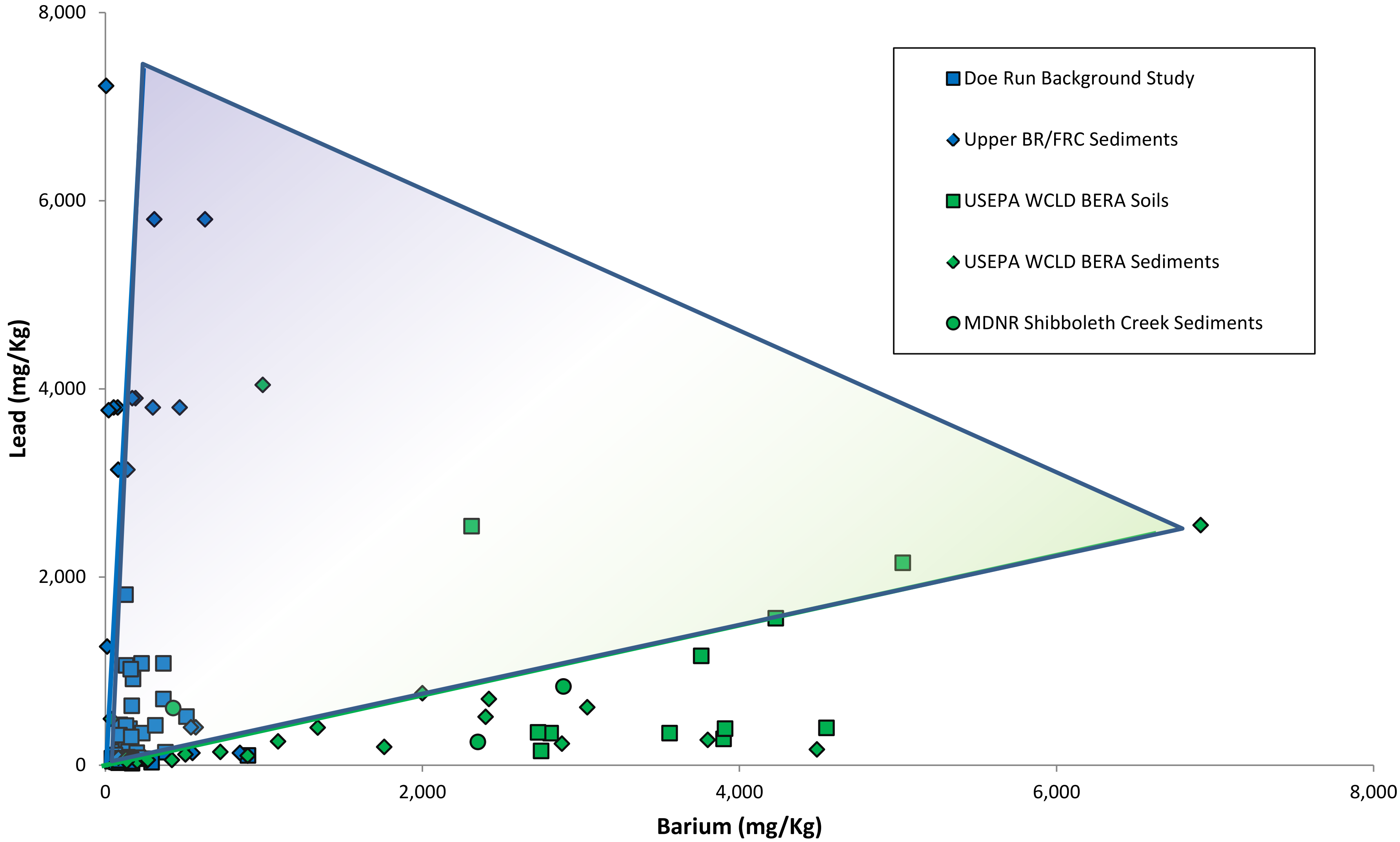

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Figure 3-5.
Lead and Barium Concentrations in Source Materials from the St. Francois Mining Area and the SE Missouri Barite District

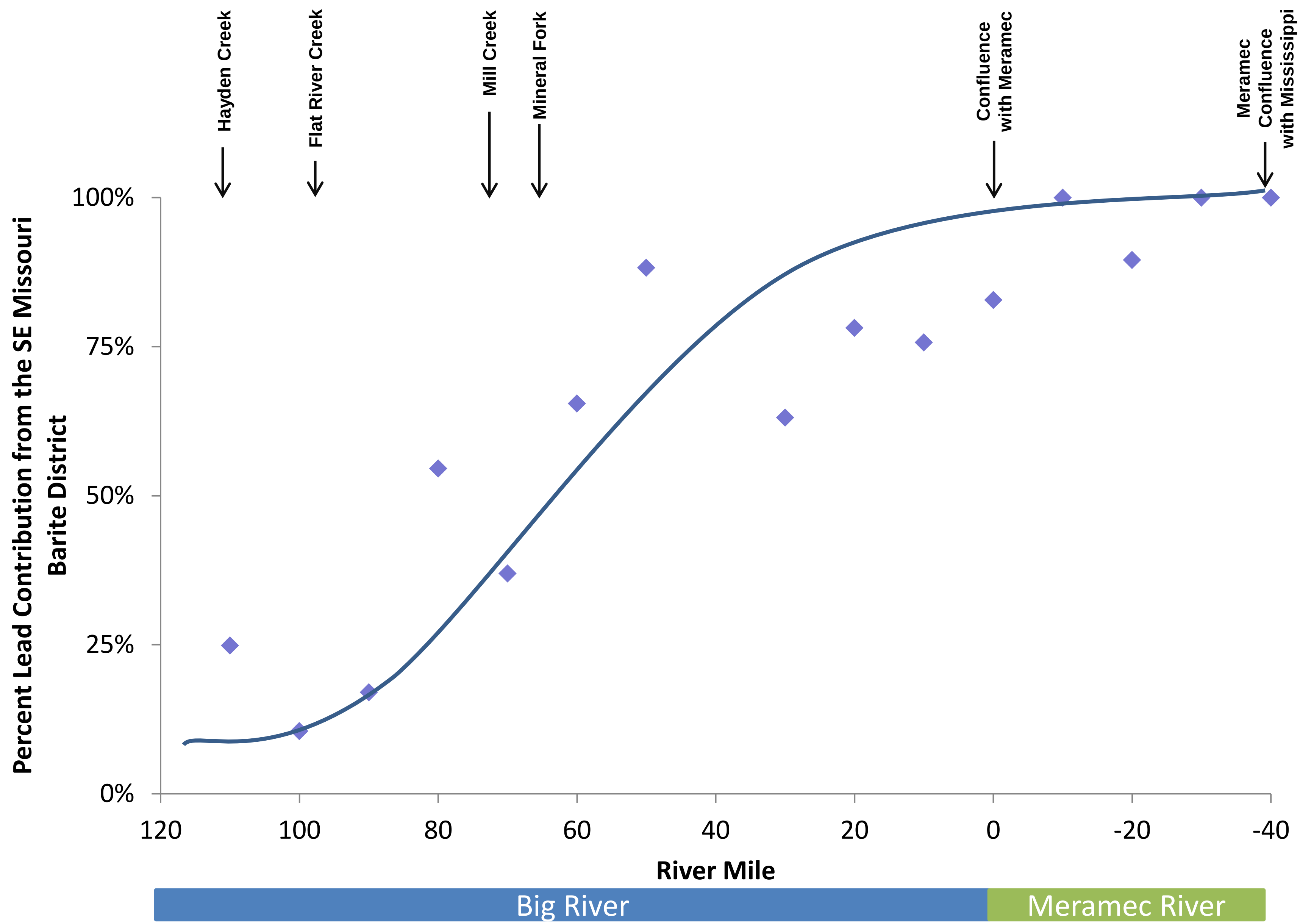

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Figure 3-6.
Lead-Barium Mixing Model Results for the Big River

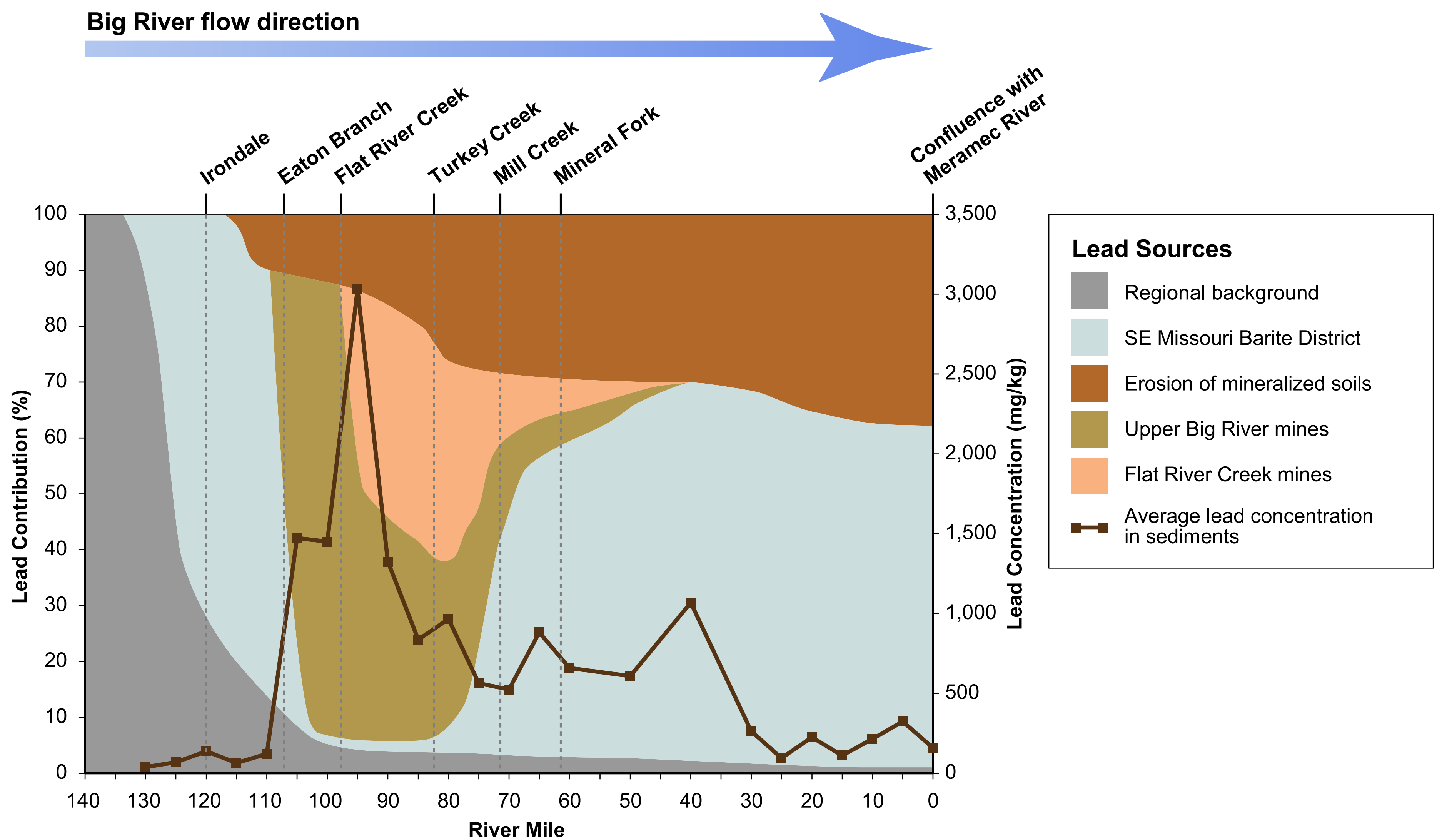

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Figure 4-1.
Estimated Lead Source Contributions to Big River Sediments

TABLES

Table 2-1. Summary of Mine Site Operations, Ownership, and Milling Byproduct Volumes

	Years of Operation[a b]		Area Covered by Milling Byproducts[a] (acres)			Volumes		
Site	Begin	End	Chat Pile	Tailings Pond	Total	Estimated Volume[b] (yd^3)	Fraction of Total Chat and Tailings in SFCMA (percent)	Ownership[a]
Sites on the Big River								
Leadwood	1894	1965	35	528	563	5,100,000	13	Doe Run (1894 to Present)
Desloge	1877	1958	95	275	370	6,500,000	17	Doe Run (1877 to Present)
Bonne Terre	1865	1961	39	306	345	5,700,000	14	Doe Run (1865 to Present)
Hayden Creek	1951	1958	--	--	--	unknown[c]	--	Doe Run (1951 to Present)
			Big River Sites Total		**1278**	**17,342,000**	**44**	
Sites on Flat River Creek								
Federal	1891	1972	43	1005	1048	5,200,000	13	ASARCO: 1891–1923 (32 years of chat and tailings production) St. Joe: 1923–1972 (49 years of tailings production) State of Missouri: (1976 to Present, 36 years)
Elvins/Rivermines	1890	1936	72	77	149	10,400,000	26	Historical Doe Run Lead Company
National	1894	1936	44	108	152	6,400,000	16	National Lead
			Flat River Creek Sites Total		**1349**	**22,000,000**	**56**	

Notes:

SFCMA = St. Francois County Mining Area

[a]Fluor Daniel (1995)

[b]NewFields (2006)

[c]No estimate provided in NewFields (2006). Volume is likely very limited considering the short, and intermittent, period of mill operation.

Table 2-2. Early Production of Lead in St. Francois, Washington, and Jefferson Counties

Date Range		Lead Production (Tons of Metal) St. Francois County	Washington County	Jefferson County
1740[a]	1799	500	9,500	--
1800	1819	3,000	17,100	200
1820	1829	4,500	10,000	1,500
1830	1849	18,000	25,000	4,680
1850	1859	8,000	13,000	3,150
1860	1869	5,000	3,000	1,400
	Total	39,000	77,600	10,930
	Extraction Losses[b]	59,091	117,576	16,561
	Smelting Losses[c]	20,091	39,976	5,631
	Total Losses	**79,182**	**157,552**	**22,191**

Notes:
Data from Winslow (1894)

[a] Lead production in Washington County began in 1725
[b]Assumes 50% ore extraction efficiency (Weigel 1953).
[c]Assumes 66% smelting efficiency.

Table 2-3. Watershed Characteristics of the Big River above Irondale, Mineral Fork, and Mill Creek

	Big River above Irondale	Mineral Fork	Mill Creek
Area (square miles)	175	190	51
Average gradient (ft/mi)	12.3	11.6	19.0

Table 2-4. Summary of Metals Concentrations in Sediments of the Washington County Lead District

Sample Location							Concentration (mg/kg)		
Name	Description	Longitude	Latitude	Study Name	Grain Size	Sample Date	Lead	Zinc	Barium
2081/2.5	Mineral Fork ab. Kingston CA	700585	4218900	MDNR WQAS[a]	NS	6/23/2009	321	394	3570
2114/0.1	Trib. To Old Mines Creek @ Hwy. 21	698559	4216812	MDNR 2009	<2mm	10/15/2009	707	1610	2940
2115/0.1	Trib to Mineral Fk. @ Dugout Rd.	699680.44	4218168	MDNR WQAS[a]	NS	8/31/2010	521	398	2400
2115/1.2	Trib. to Mineral Fk. @ Hwy 21	700455.24	4216693.2	MDNR WQAS[a]	NS	9/21/2010	329	525	1640
2118/3.2	Mill Cr. @Tiff,Mo.	706224	4210139	MDNR WQAS[a]	NS	6/23/2009	487	1070	5920
Fountain Farm Branch #1	Upstream Confluence with Mill Creek	702139	4205858	MDNR 2009	<2mm	10/15/2009	237	606	1930
MF02	Mineral Fork - on tributary west of Big River	702025	4219515	USEPA 2006	NS	9/1/2005	40.7	88.4	--
MF02	Mineral Fork - on tributary west of Big River	702025	4219515	USEPA 2006	<0.5mm	9/1/2005	912	316	--
Mill_Creek-Bar-89	Access Point = Mill Ck at Tiff	706258.83	4210241.3	Pavlowsky et al. 2010	<2mm	1/22/2009	105	314	--
Mill_Creek-Bar-90	Access Point = Mill Ck at Tiff	706272.3	4210272.5	Pavlowsky et al. 2010	<2mm	1/22/2009	ND	214	--
Mill_Creek-Bar-94	Access Point = Upper Mill Cr- control	699923.14	4202676.2	Pavlowsky et al. 2010	<2mm	1/22/2009	306	1338	--
Mill_Creek-Glide-61	Access Point = Upper Mill Cr.	706263.95	4210277.8	Pavlowsky et al. 2010	<2mm	1/22/2009	67	316	--
Mill_Creek-Glide-62	Access Point = Upper Mill Cr.	706268.55	4210278.7	Pavlowsky et al. 2010	<2mm	1/22/2009	79	368	--
Mineral_Fork_Creek-Bar-67	Access Point = Mineral Fork at Tiff	700581.75	4218648.7	Pavlowsky et al. 2010	<2mm	1/19/2009	78	133	--
Mineral_Fork_Creek-Bar-68	Access Point = Mineral Fork at Tiff	700590.44	4218662	Pavlowsky et al. 2010	<2mm	1/19/2009	38	88	--
Mineral_Fork_Creek-Glide-56	Access Point = Mineral Fork	700598.44	4218703.7	Pavlowsky et al. 2010	<2mm	1/20/2009	106	168	--
Mineral_Fork_Creek-Glide-57	Access Point = Mineral Fork	700594.53	4218704.2	Pavlowsky et al. 2010	<2mm	1/20/2009	105	139	--
Pond Creek #1	Upstream Confluence with Mill Creek	704868	4205941	MDNR 2009	<2mm	10/15/2009	96.8	525	1460
Pond Creek #2	Downstream Pond Creek Rd.	703719	4203308	MDNR 2009	<2mm	10/15/2009	46.6	488	1580
Salt Pines Creek #1	North/Downstream of MO Hwy 21	697830	4215928	MDNR 2009	<2mm	10/15/2009	660	1220	3050
SD01	Pond SE of Potosi	692624.18	4200359.5	USEPA 2008	NS	12/1/2008	4040	193	994
SD02	Pond N of Potosi	695699.38	4203148.7	USEPA 2008	NS	12/1/2008	2550	770	6910
SD03	Mill Creek	700563.21	4203901.4	USEPA 2008	NS	12/1/2008	266	688	3800
SD04	Mill Creek	700208.81	4202065.3	USEPA 2008	NS	12/1/2008	140	338	726
SD05	Pond Creek	704728.45	4203563.2	USEPA 2008	NS	12/1/2008	54.3	172	420
SD06	Confluence of Mill and Pond Creeks	704992.87	4206038.9	USEPA 2008	NS	12/1/2008	99.4	276	898
SD07	Mill Creek Upstream of Shibboleth Branch	706145.3	4210193	USEPA 2008	NS	12/1/2008	49	182	262
SD08	Mill Creek Downstream of Shibboleth Branch	706373.78	4210556.6	USEPA 2008	NS	12/1/2008	53.2	178	269
SD09	Mill Creek	705357.94	4207723.1	USEPA 2008	NS	12/1/2008	37.5	131	201
SD10	Mill Creek upstream of confluence with the Big River	708522.11	4212129.9	USEPA 2008	NS	12/1/2008	38.7	141	136
SD11	Shibboleth Branch	702620.15	4209860	USEPA 2008	NS	12/1/2008	70.8	162	131
SD12	Mine a Breton Creek downstream of Potosi	693996.85	4201488.3	USEPA 2008	NS	12/1/2008	614	436	3040
SD13	Bates Creek (tributary to Mine a Breton Cr)	692746.33	4201726	USEPA 2008	NS	12/1/2008	193	298	1760
SD14	Pond N of Potosi	695379.07	4203001.1	USEPA 2008	NS	12/1/2008	228	283	2880
SD15	Keyes Branch	699655.98	4205154.3	USEPA 2008	NS	12/1/2008	703	609	2420
SD16	Pond Hollow	699597.96	4205589.5	USEPA 2008	NS	12/1/2008	397	650	1340
SD17	Pond Creek	703737.47	4203252	USEPA 2008	NS	12/1/2008	763	604	2000
SD18	Shibboleth Branch	705386.1	4210860.9	USEPA 2008	NS	12/1/2008	113	304	506
SD19	Shibboleth Branch	706142.1	4210312.1	USEPA 2008	NS	12/1/2008	251	608	1090
SD20	Pond Creek	703075.07	4202287.9	USEPA 2008	NS	12/1/2008	167	611	4490
SD22	Tributary to Mill Creek	700270.95	4205912.1	USEPA 2008	NS	12/1/2008	513	598	2400
SEMO-8	Mineral Fork Creek near mouth	700641.4	4218872.5	Besser et al. 2009	<0.25mm	9/10/2008	200	190	--
SEMO-8	Mineral Fork Creek near mouth	700641.4	4218872.5	Besser et al. 2009	<2mm	9/10/2008	110	190	--

Table 2-4. Summary of Metals Concentrations in Sediments of the Washington County Lead District

Sample Location							Concentration (mg/kg)		
Name	Description	Longitude	Latitude	Study Name	Grain Size	Sample Date	Lead	Zinc	Barium
SEMO-8	Mineral Fork Creek near mouth	700641.4	4218872.5	Besser et al. 2009	<2mm	9/10/2008	61	42	--
Shibboleth Branch #1	Downstream brdge Johnson Rd.	705671	4210490	MDNR 2009	<2mm	10/15/2009	607	553	428
Shibboleth Branch #2	End Johnson Rd.	704807	4210506	MDNR 2009	<2mm	10/15/2009	246	845	2350
Shibboleth Branch #3	Approx. 0.25 miles E of Hwy E, Powder Lake Spring Rd.	702030	4209388	MDNR 2009	<2mm	10/15/2009	836	697	2890
Summary Statistics						Average	405	448	2025
						Geometric mean	197	340	1323

Notes:

NS = not specified

[a]Data Compilation from MDNR Water Quality Assessment System - Big River Watershed. Available at: http://www.dnr.mo.gov/mocwis_public/wqa/waterbodySearch.do. Missouri Department of Natural Resources, Jefferson City, MO

Table 2-5. Concentrations of Barium, Lead, and Zinc in Sediments Upstream of the St. Francois County Mining Area

Sample Location							Concentration (mg/kg)		
Name	Description	Longitude	Latitude	Study Name	Grain Size	Sample Date	Lead	Zinc	Barium
2080/65.5	Big River at Irondale	703232	4189466	MDNR WQAS[a]	NS	9/1/2000	2357	106.3	--
2080/65.5	Big River at Irondale	703232	4189466	MDNR WQAS[a]	NS	2/23/1988	58	110	620
2080/65.5	Big River at Irondale	703232	4189466	MDNR WQAS[a]	NS	9/13/1989	89	61	840
Big River #9	Upstream Control - Upstream All; Irondale, MO, Washington Co.	703859.64	4189946.5	MDNR WQAS[a]	< 2mm	10/1/2002	20.1	18.1	--
Big River #9	Upstream Control - Upstream All; Irondale, MO, Washington Co.	703859.64	4189946.5	MDNR WQAS[a]	< 2mm	10/1/2002	15.8	17.9	--
Big River #9	Upstream Control - Upstream All; Irondale, MO, Washington Co.	703859.64	4189946.5	MDNR WQAS[a]	< 2mm	10/1/2002	14.7	18.9	--
Big_River-Bar-25	Access Point = Hwy U at Irondale-control	703194.77	4189488.1	Pavlowsky et al. 2010	< 2mm	11/23/2008	ND	21	--
Big_River-Bar-26	Access Point = Hwy U at Irondale-control	703194.25	4189487.9	Pavlowsky et al. 2010	< 2mm	11/23/2008	ND	17	--
Big_River-Bar-58	Access Point = Hwy 8 above Leadwood-control	707622.77	4193767.9	Pavlowsky et al. 2010	< 2mm	1/19/2009	ND	39	--
Big_River-Glide-25	Access Point = Hwy U at Irondale-control	703171.08	4189494.5	Pavlowsky et al. 2010	< 2mm	10/23/2008	ND	26	--
Big_River-Glide-26	Access Point = Hwy U at Irondale-control	703172.4	4189498.6	Pavlowsky et al. 2010	< 2mm	10/23/2008	ND	20	--
Big_River-Glide-48	Access Point = Hwy 8 above Leadwood-control	707624.79	4193762.5	Pavlowsky et al. 2010	< 2mm	1/19/2009	ND	47	--
BKG11	Background, Big River upstream of Leadwood Pile	707588	4193694	USEPA 2006	NS	9/1/2005	432	206	--
BR_aboveIrondale	Big River above Irondale below Cedar River	701520.99	4187539.6	Roberts et al. 2009	< 0.25mm	9/1/2007	17	18	--
BR_aboveIrondale	Big River above Irondale below Cedar River	701520.99	4187539.6	Roberts et al. 2009	< 2mm	9/1/2007	15		--
BR_belowHwy8	Big River below Hwy 8 above Leadwood	707621.73	4193750	Roberts et al. 2009	< 0.25mm	9/1/2007	22	24	--
BR_belowHwy8	Big River below Hwy 8 above Leadwood	707621.73	4193750	Roberts et al. 2009	< 2mm	9/1/2007	20	32	--
BR-1	Big River, upper reaches, riffle	696139.82	4187340	Zachritz 1978	< 177µm	4/8/1978	65	16.4	--
BR-1	Big River, upper reaches, riffle	696139.82	4187340	Zachritz 1978	< 177µm	5/15/1978	94	283	--
BR-1	Big River, upper reaches, riffle	696139.82	4187340	Zachritz 1978	< 177µm	5/30/1978	72	233	--
BR-1	Big River, upper reaches, riffle	696139.82	4187340	Zachritz 1978	< 177µm	6/20/1978	148	646	--
BR-1	Big River, upper reaches, riffle	696139.82	4187340	Zachritz 1978	< 177µm	6/30/1978	111	507	--
BR-2	Big River, upper reaches, riffle	707605.89	4193717.2	Zachritz 1978	< 177µm	4/8/1978	37	49	--
BR-2	Big River, upper reaches, riffle	707605.89	4193717.2	Zachritz 1978	< 177µm	5/15/1978	15.2	50	--
BR-2	Big River, upper reaches, riffle	707605.89	4193717.2	Zachritz 1978	< 177µm	5/30/1978	59	72	--
BR-2	Big River, upper reaches, riffle	707605.89	4193717.2	Zachritz 1978	< 177µm	6/20/1978	36	72	--
BR-2	Big River, upper reaches, riffle	707605.89	4193717.2	Zachritz 1978	< 177µm	6/30/1978	24	34	--
C1	Route U bridge, SW of Irondale, MO	703214	4189506	MDNR 2007	< 2mm	11/7/2007	36.02	53.38	--
C1	Route U bridge, SW of Irondale, MO	703214	4189506	MDNR 2007	2-12.5mm	11/7/2007	31.73	51.64	--
C1	Route U bridge, SW of Irondale, MO	703214	4189506	MDNR 2007	> 12.5mm	11/7/2007	18.89	28.61	--
C2	MO Hwy 21 bridge at Bootleg Conservation Area	696005	4187249	MDNR 2007	< 2mm	11/7/2007	23.07	53.7	--
C2	MO Hwy 21 bridge at Bootleg Conservation Area	696005	4187249	MDNR 2007	2-12.5mm	11/7/2007	20.33	30.99	--
C2	MO Hwy 21 bridge at Bootleg Conservation Area	696005	4187249	MDNR 2007	> 12.5mm	11/7/2007	10.94	26.46	--
C3	Route C bridge at Belgrade, MO	690006	4184011	MDNR 2007	< 2mm	11/7/2007	54.16	49.34	--
C3	Route C bridge at Belgrade, MO	690006	4184011	MDNR 2007	2-12.5mm	11/7/2007	37.19	40.85	--
C3	Route C bridge at Belgrade, MO	690006	4184011	MDNR 2007	> 12.5mm	11/7/2007	21.81	25.66	--
ID	Big River -Cedar Creek (Reference (CERC #1)	701520.99	4187539.6	Roberts et al. 2009	< 2mm	9/1/2008	15	17	215
SEMO-1	Big River above Irondale	701756.14	4188208.4	Besser et al. 2009	< 2mm	9/9/2008	11	5.7	--
SEMO-1	Big River above Irondale	701756.14	4188208.4	Besser et al. 2009	< 2mm	9/9/2008	8	20	--
SEMO-1	Big River above Irondale	701756.14	4188208.4	Besser et al. 2009	< 0.25mm	9/9/2008	36	20	--
SEMO-1	Big River above Irondale	701756.14	4188208.4	Allert et al. 2010	< 2mm	7/12/2008	11	6	--
SEMO-1	Big River above Irondale	701756.14	4188208.4	Allert et al. 2010	< 2mm	7/12/2008	7.9	20	40
SEMO-22	Reference site, Hwy U	703542.09	4189501.6	Allert et al. 2010	< 2mm	7/12/2008	14	5.44	40

Table 2-5. Concentrations of Barium, Lead, and Zinc in Sediments Upstream of the St. Francois County Mining Area

Sample Location							Concentration (mg/kg)		
Name	Description	Longitude	Latitude	Study Name	Grain Size	Sample Date	Lead	Zinc	Barium
SEMO-22	Reference site, Hwy U	703542.09	4189501.6	Allert et al. 2010	< 2mm	7/12/2008	10.5	21	--
Site 1	Big River at Irondale	696139.29	4187383.1	NewFields 2006	NS	9/16/1999	75	91	--
Summary Statistics						Average	107	75	351
						Geometric mea	33	38	178

Notes:

ND = nondetect

NS = not specified

[a]Data Compilation from MDNR Water Quality Assessment System - Big River Watershed. Available at: http://www.dnr.mo.gov/mocwis_public/wqa/waterbodySearch.do. Missouri Department of Natural Resources, Jefferson City, MO

Table 3-1. Concentrations of Barium, Lead, and Zinc in Floodplain Cores from St. Francois and Washington State Parks

	Coordinates (UTM Zone 15)				Concentration (mg/kg)[a]		
Core	Easting	Northing	Sample ID	Sample Interval (ft)	Barium	Lead	Zinc
SF-SB1	716084.3	4204123	SF-SB1-0-1-N	0-1	196	663	237
			SF-SB1-1-2-N	1-2	228	376	121
			SF-SB1-2-3-N	2-3	--	--	--
			SF-SB1-3-4-N	3-4	109	7000	934
			SF-SB1-4-5-N	4-5	--	--	--
			SF-SB1-5-6-N	5-6	197	621	49.4
			SF-SB1-6-7-N	6-7	146	1030	100
			SF-SB1-7-8-N	7-8	--	--	--
			SF-SB1-8-9-N	8-9	121	92.9	46.4
			SF-SB1-9-10-N	9-10	--	--	--
			SF-SB1-10-11-N	10-11	--	--	--
			SF-SB1-11-12-N	11-12	124	39.5	38.2
			SF-SB1-12-13-N	12-13	--	--	--
			SF-SB1-13-14-N	13-14	--	--	--
			SF-SB1-14-15-N	14-15	--	--	--
			SF-SB1-15-16-N	15-16	--	--	--
			SF-SB1-16-17-N	16-17	--	--	--
			SF-SB1-17-18-N	17-18	--	--	--
			SF-SB1-18-19-N	18-19	56.2	20.4	28.6
			SF-SB1-19-20-N	19-20	--	--	--
SF-SB3	716047	4204111	SF-SB3-0-1-N	0-1	64.9	914	445
			SF-SB3-1-2-N	1-2	--	--	--
			SF-SB3-2-3-N	2-3	123	964	495
			SF-SB3-3-4-N	3-4	--	--	--
			SF-SB3-4-5-N	4-5	--	--	--
			SF-SB3-5-6-N	5-6	--	--	--
			SF-SB3-6-7-N	6-7	--	--	--
			SF-SB3-7-8-N	7-8	--	--	--
			SF-SB3-8-9-N	8-9	--	--	--
			SF-SB3-9-10-N	9-10	--	--	--
			SF-SB3-10-11-N	10-11	--	--	--
			SF-SB3-11-12-N	11-12	--	--	--
			SF-SB3-12-13-N	12-13	63.6	2440	1110
			SF-SB3-13-14-N	13-14	81.5	4480	775
			SF-SB3-14-15-N	14-15	111	1890	664
			SF-SB3-15-16-N	15-16	--	--	--
			SF-SB3-16-17-N	16-17	--	--	--
			SF-SB3-17-18-N	17-18	71	2670	1240
WA-SB1	703316.7	4217093	WA-SB1-0-1-N	0-1	1040	1720	525
			WA-SB1-1-2-N	1-2	1680	1410	436
			WA-SB1-2-3-N	2-3	--	--	--
			WA-SB1-3-4-N	3-4	269	230	121
			WA-SB1-4-5-N	4-5	--	--	--
			WA-SB1-5-6-N	5-6	--	--	--
			WA-SB1-6-7-N	6-7	--	--	--
			WA-SB1-7-8-N	7-8	250	34.7	95.1
			WA-SB1-8-9-N	8-9	--	--	--
			WA-SB1-9-10-N	9-10	--	--	--
			WA-SB1-10-11-N	10-11	--	--	--
			WA-SB1-11-12-N	11-12	--	--	--
			WA-SB1-12-13-N	12-13	17.4	9	35.3
			WA-SB1-13-14-N	13-14	--	--	--

Table 3-1. Concentrations of Barium, Lead, and Zinc in Floodplain Cores from St. Francois and Washington State Parks

	Coordinates (UTM Zone 15)				Concentration (mg/kg)[a]		
Core	Easting	Northing	Sample ID	Sample Interval (ft)	Barium	Lead	Zinc
WA-SB3	703301.5	4217988	WA-SB3-0-1-N	0-1	923	1800	479
			WA-SB3-1-2-N	1-2	987	1810	490
			WA-SB3-2-3-N	2-3	--	--	--
			WA-SB3-3-4-N	3-4	--	--	--
			WA-SB3-4-5-N	4-5	1500	1580	411
			WA-SB3-5-6-N	5-6	--	--	--
			WA-SB3-6-7-N	6-7	--	--	--
			WA-SB3-7-8-N	7-8	283	168	113
			WA-SB3-8-9-N	8-9	--	--	--
			WA-SB3-9-10-N	9-10	--	--	--
			WA-SB3-10-11-N	10-11	326	319	125
			WA-SB3-11-12-N	11-12	158	43.9	61.1
			WA-SB3-12-13-N	12-13	--	--	--
			WA-SB3-13-14-N	13-14	--	--	--
			WA-SB3-14-15-N	14-15	--	--	--
			WA-SB3-15-16-N	15-16	--	--	--

Notes:

-- Interval not analyzed.

[a] Samples analyzed using EPA Methods 3050B/6010B.

Table 4-1. Estimated Source Contributions of Lead to Big River Sediments

		Estimated Contribution of Lead Mass			
		Big River at Downstream End of the SFCMA		Lower Big River	
Source/Site	Responsible Party	Lower (percent)	Upper (percent)	Lower (percent)	Upper (percent)
Erosion of Mineralized Soils (both surface mined areas and undisturbed soils)	None	10	30	10	40
Desloge Chat Release (1977)	Unclear	de minimus	20	0	0
Flat River Creek[a]	Multiple parties	40	60	0	de minimis
Upper Big River	Doe Run	40	60	0	de minimis
Railroad Ballast	Union Pacific Railroad	de minimus	50 (localized)	0	0
SE Missouri Barite District	Multiple parties, not including Doe Run	de minimus	10	60	90

Notes:

SFCMA = St. Francois County Mining Area

[a]Based on years of ownership and operation, weighted for the volume of chat and/or tailings at the site.

APPENDIX A

BIG RIVER WATERSHED MODEL SUMMARY

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MEMORANDUM - Draft

To:	Chris Neaville and Mike Montgomery
From:	Marcia Greenblatt and Mike Ruby
Date:	October 7, 2013
Subject:	Big River Watershed Model Summary

INTRODUCTION

An evaluation was performed to estimate watershed soil loading and associated lead loading to Big River.

OVERVIEW OF APPROACH

Sediment loads to Big River were estimated using the Universal Soil Loss Equation (USLE; Renard et al. 1997). The USLE calculations were developed through an integrated ArcGIS-based analysis using publically available land cover, soil, precipitation, and elevation data for the watershed. The application of the USLE model, including selection of model parameters, followed the methods developed and applied by Montana Department of Environmental Quality (DEQ) (2012) to develop a sediment total maximum daily load (TMDL). The resultant Big River sediment loads were compared with available, relevant, regional sediment load data for verification of the estimates.

Lead loads were estimated by assigning soil lead concentrations to sediment load estimates. Soil lead concentrations were developed from available background soil data and were assigned based on geology and mining activity history.

DATA SOURCES AND APPROACH

Data available from the public domain were compiled for the Big River watershed to support the USLE calculations. The following summarizes the data sources used for the USLE analyses.

Delineation of Stream Subbasins

The ArcHydro extension in the ArcGIS software package was used to delineate the drainage catchment areas smaller than the Hydrologic Unit Code (HUC) 12 basins acquired from the National Hydrologic Dataset (NHD). The 10-meter digital elevation model (DEM) grid developed from the U.S. Geological Survey (USGS) National Elevation Dataset (USGS 2011) was used as input to produce a flow direction grid based on the ground surface topography. The flow direction grid was defined by slopes calculated using an eight-direction pour point model (Maidment 2002). The flow direction grid was in turn used as input to produce a flow accumulation grid, which records the number of cells that drain to a specific cell in the grid. The drainage subbasins are defined from a stream definition grid with the use of a threshold drainage area value, resulting in subbasin catchment areas.

Estimated Soil Loss with Revised Universal Soil Loss Equation (USLE)

Soil loss due to runoff and erosion was estimated for each of the stream subbasins based on the USLE. The USLE estimates the annual soil loss (A) based on five factors using the following equation:

$$A = R\ x\ K\ x\ LS\ x\ C\ x\ P$$

Each of the five factors is described below, and associated shapefiles are listed in Table 1:

- **R-Factor (Rainfall Erosivity):** Isoerodent contours produced by the U.S. Department of Agriculture (USDA) were used to estimate the R-Factor on a 1,000-m grid across the continental United States, as shown in the U.S. Environmental Protection Agency publication Fact Sheet 3.1 (USEPA 2012). A digital version of the isoerodent contours was acquired from the National Center for Ecological Analysis and Synthesis (NCEAS 2011). The grid was resampled to 10 m for the USLE calculation.
- **K-Factor (Soil Erodibility):** Federal engineering guidance (SCS 1983) was followed to develop the K-value soil classifications from the National Cooperative Soil Survey database (NRCS 2012). Soil K-value classifications were determined by guidance from the National Oceanic and Atmospheric Administration (NOAA 2004). Soils high in clay generally are characterized by low K-Factors because of resistance to detachment. Areas missing K-Factors in the tabular data were given the average K-Factor of the matching soil type from another county within the study area. The remaining areas missing K-Factors (water, pits, dumps, etc.) were given a value of 0.2, the lowest K-Factor value in the study area.
- **LS-Factor (Slope Length):** The USGS DEM (USGS 2011) was used to derive the slope lengths. The DEM was processed using a methodology consistent with that outlined

by Van Remortel et al. (2004). The output is length in meters from the top of slope to the lower end of the segment.

- **C-Factor (Cover Management):** The 2006 National Land Cover Dataset (NLCD; MRLC 2006) was used to establish the influence of different cover types on erosion. NLCD classes were reclassified to C-Factor values as specified in Montana DEQ (2012). A C-Factor of 0.001 was assumed for "Open Water" and "Developed, High Intensity."
- **P-Factor (Erosion Control Practice):** The P-Factor represents the ratio of soil loss by certain crop support practices compared to straight row farming. This factor is not relevant to the soil erosion analyses presented herein and was set to a value of 1 (Montana DEQ 2012).

The 970-mi^2 watershed was gridded into a series of 10-m^2 cells, and each of the above factors was estimated for each grid cell. The USLE model was then used to calculate the annual soil erosion for each grid cell.

Table 1. ArcGIS Shapefiles and Raster Grids for the USLE Evaluation

GIS Layer	File Name	File Type
R-factor	r_fact_10m	Raster
K-factor	k_fact_10mnew	Raster
LS-factor	ls_fact_10m	Raster
C-factor	c_fact_10m	Raster
USLE Results	USLE_10mnew	Raster
Big River Subbasins	wbdhu12_a_mo.shp	Shapefile
Geology	Bonneterre_and_Davis_Combined_20130820.shp	Shapefile
Geology Contact Buffer	Bonneterre_Davis_Contact_Buffer_600m.shp	Shapefile
Historic Mining	WCLD_Historic_Mining_Activity.shp	Shapefile
WCLD Boundary	WCLD_boundary.shp	Shapefile
Zones	Big_River_HUC12_Zonal_Dissolve.shp	Shapefile
Union for Zonal Stats	Master_Zonal_Shape_Final.shp	Shapefile

Sediment Delivery Ratio

The USLE model provides an estimate of soil erosion for a given slope. However, the majority of this eroded soil is redeposited where runoff is insufficient to maintain soil particles in suspension with downstream flow. Therefore, only a portion of the eroded soil in a subbasin is delivered as sediment downstream, and a sediment delivery ratio (SDR) is commonly used to account for the soil that is ultimately delivered from a drainage area to the river (SCS 1983). Redeposition of eroded soil increases with the size of the drainage area and was calculated following USAD0ARE-S-40 (Boyce 1975):

$$SDR=0.31*A^{-0.3}$$

Where A is the subbasin area in square miles.

The SDR was estimated for each subbasin, and ranged from 9 to 13 percent. The resulting sediment load was calculated as the product of the soil load estimated by USLE and the SDR.

Estimated Lead Loads

Soil lead concentrations were assigned to areas (referred to as soil erosion areas) delineated based on geology and historical mining activities (Table 2). An evaluation of background soil lead data has indicated a strong relationship between underlying geology and soil lead concentrations. Specifically, the highest soil lead concentrations were generally observed in an area around the contact between the Bonneterre dolomite and the Davis shale formations. This Bonneterre-Davis contact zone appears to extend approximately 600 meters on either side of the contact. Elevated lead concentrations were also observed in soils overlying the Bonneterre and Davis formations, although these were generally somewhat lower than those observed in the contact zone. Elevated soil lead concentrations were also observed throughout the Southeast MO Barite mining district[1] within Washington County.

Historical surficial mining in the Southeast MO Barite district was comprised of two technologically defined eras. The first era, the hand mining era, began in 1720 with the first lead mining and continued through the 1920s with barite mining. From the 1930s through the 1990s barite was extracted using mechanized equipment. The extent of mechanized barite mining was estimated for 1955 from aerial photos (obtained from USDA-Farm Service Agency), in combination with the Inventory of Mines, Opportunities, and Prospects (IMOP) database. This analysis indicated that approximately 16 mi^2 of land in the S.E. MO Barite District were actively being mined for barite in 1955. Delineation of these areas was intended to provide a snapshot in time of disturbed land, rather than an estimation of all areas disturbed over the 300 year mining history in the area.

Soil lead concentrations for each soil erosion area were assigned as the average value of the available data within each area. Data used in the evaluation included relevant USGS and

[1] The boundaries of the S.E. MO Barite district, as represented by the shape file called "WCLD_boundary.shp" was delineated by identifying the most dense area of lead and barium mines in the Washington County area as identified by the IMOP Database (MDNR, 2008)

USEPA datasets and from the background lead study performed by Doe Run (Integral 2013). Soil lead loads were calculated for each subbasin and each soil erosion area as the product of the estimated sediment load and the soil lead concentration.

Table 2. Soil Lead Concentrations

Soil Erosion Area	Estimated Soil Lead Concentration (mg/kg)
Soils overlaying Davis shale	333
Soils overlaying Bonneterre dolomite	369
Davis-Bonneterre Contact Zone	1055
Southeast MO Barite District	1035
Regional background	60
Areas of mechanized barite mining	714

SEDIMENT LOAD RESULTS

Estimated sediment loads from watershed soil runoff were calculated at several locations within the Big River watershed (Figure 1) by summing the loads from individual subbasins (Table 3)[2]. The estimated sediment loads were compared to available relevant information to provide verification of the order-of-magnitude estimates:

1. **Sediment load estimates for USGS Gage Station 07017610, Big River below Bonne Terre, Missouri.** Suspended sediment data have been collected at this location since 2011, and USGS has estimated daily sediment discharge for the 2012 water year (USGS 2013). These daily values were summed up, and compared to the annul sediment load estimated by the USLE model (Table 4). The sediment loads estimated from the USGS data are lower than the USLE result; however, they are based on only one year of data. Additionally, rainfall in 2012 was below average, with limited high flow events expected to carry the majority of the sediment load. The fact that the two estimates are within a factor of 2 suggest that the USLE model provides a reasonable order-of-magnitude estimate of sediment loads.

2. **Annul sediment loads in proximate Missouri streams.** USGS used available suspended sediment data for selected Lower Missouri River and tributary gaging stations to estimate annual suspended sediment loads (Heimann et al. 2010). Estimated annual sediment loads from tributaries near the Big River watershed were normalized to the watershed area for comparison with the normalized Big River

[2] Sediment loads are expressed in metric tons/year

estimated loads (Table 5). Tributaries were selected that are within watersheds that have similar topographic features and land use patterns to Big River. The normalized sediment loads for Big River are within the range of those estimated by USGS for nearby streams.

Table 3. Estimated Sediment Loads

Location	Estimated Sediment Load (ton/yr)
Confluence of Big River and Flat River Creek	11,000
Confluence of Big River and Turkey Creek	16,400
Confluence of Big River and Mineral Fork	29,200
Big River Watershed	44,600

Table 4. Comparison of USLE Sediment Load Estimated with USGS Sediment Load Estimate

Location	Estimated Sediment Load (ton/yr)
Confluence of Big River and Turkey Creek	16,400
USGS Sediment Rating Curve Study – USGS 07017610, Big River Below Bonne Terre; WY 2011-2012, estimated load	9,100

Table 5. Comparison of Normalized Sediment Loads

Location	Area (mi^2)	Normalized Sediment Load (tons/yr-mi^2)
Confluence of Big River and Flat River Creek	264	42
Confluence of Big River and Turkey Creek	401	41
Confluence of Big River and Mineral Fork	720	41
Big River Watershed	970	46
06933500 Gasconade River at Jerome, Missouri[a]	2840	64
06926510 Osage River at St. Thomas, Missouri[a]	14,584	44

Notes:
[a]Heimann et al. (2010)

LEAD LOAD RESULTS

Lead loads for each soil erosion area were calculated for several locations within the watershed (Table 6). These loads represent the current estimated average annual loads of lead entering Big River from the different soil erosion areas within the watershed. The regional soils area includes all areas outside of the Bonneterre-Davis Contact Zone, the Bonneterre and Davis units, and the Southeast MO Barite District.

A model scenario was also performed to estimate lead loading due to increased soil erosion during the mechanized barite mining era in the S.E. MO Barite District. As discussed above, approximately 16 mi^2 were identified as being disturbed, and these areas were assigned a cover management factor (C) value representative of highly disturbed land. These areas were assigned a soil lead concentration based on relevant soil lead data (Integral 2013). The estimated lead load from these areas (Table 6) represents lead associated with soil runoff, and does not include any loading resulting directly from the mining activities.

Table 6. Watershed Lead Loading Results

	Soil Lead Loading (kg/yr)		
Area of Soil Erosion	Confluence of Big River and Flat River Creek	Confluence of Big River and Mineral Fork	Big River Watershed
Bonneterre-Davis Contact Zone Soils	1,700	2,600	2,600
Soils Overlying Bonneterre and Davis Units	600	1,500	1,500
Southeast MO Barite District Soils	--	7,500	9,900
Regional Soils	500	900	1,700
Mechanized barite mining	--	12,800	16,600

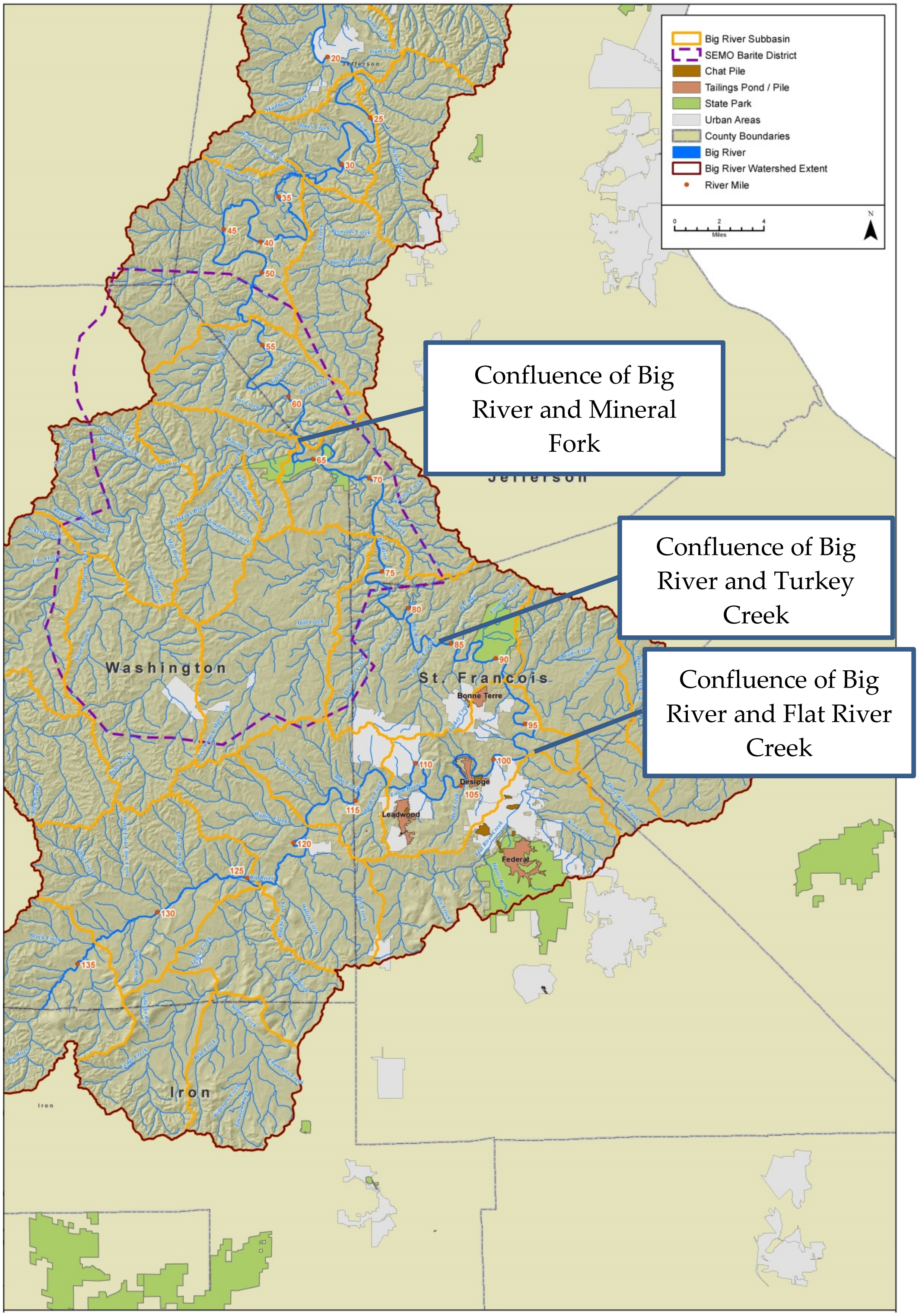

Figure 1. Locations of Model Results

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