

Prepared in cooperation with the U.S. Environmental Protection Agency, Region 7

# Surface-Water Quality and Suspended-Sediment Quantity and Quality within the Big River Basin, Southeastern Missouri, 2011–13



Scientific Investigations Report 2015–5171

U.S. Department of the Interior U.S. Geological Survey

**Front cover photographs:** Left, baseflow sample collection by wading. Center, turbidity sensor equipped with a wiper to reduce sensor fouling. Right, stormflow event sampling from bridge.

**Back cover photographs:** Top, streamflow measuring during a large stormflow event at the upstream site. Center, turbidity sensor equipped with a wiper to reduce sensor fouling. Bottom, sediment sample processing at the Missouri Water Science Center Sediment Laboratory.

**Background photograph:** Large stormflow event during study period at the Byrnesville downstream site.

By Miya N. Barr

Prepared in cooperation with the U.S. Environmental Protection Agency, Region 7

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U.S. Department of the Interior U.S. Geological Survey

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Suggested citation:

Barr, M.N., 2016, Surface-water quality and suspended-sediment quantity and quality within the Big River Basin, southeastern Missouri, 2011–13: U.S. Geological Survey Scientific Investigations Report 2015–5171, 39 p., http://dx.doi.org/10.3133/sir20155171.

ISSN 2328-0328 (online)

# Contents

Abstract	1
Introduction	2
Study Background	2
Purpose and Scope	4
Description of Study Area	4
Methods	5
Field Methods	5
Laboratory Methods	7
Quality Assurance and Quality Control	7
Data Analysis and Reporting	9
Surface-Water Quality	13
Streamflow Conditions	13
Continuous Water Quality	14
Suspended-Sediment Quantity	19
Daily Suspended-Sediment Concentrations and Loads	22
Event-Based Suspended-Sediment Concentrations, Load, and Yields	24
Suspended-Sediment Quality	25
Selected Trace-Element Concentrations in Suspended Sediments	25
Event-Based Loads and Yields of Selected Trace-Element Concentrations in	
Suspended Sediments	31
Summary	36
References Cited	38

# Figures

<ol> <li>Graphs showing turbidity duration curves for two study sites on the Big River, Missouri, October 2011–September 2013</li></ol>	3
<ol> <li>Graphs showing instantaneous turbidity in relation to discrete suspended-sediment concentrations used to develop a regression model for the computation of daily suspended-sediment concentrations and loads for two study sites on the Big River, October 2011–September 2013</li></ol>	9
<ol> <li>Graphs showing daily mean streamflow in relation to discrete suspended-sediment concentrations used to develop a regression model for the computation of estimated daily suspended-sediment concentrations and loads for two study sites on the Big River, Missouri, October 2011–September 2013</li> <li>Graph showing total monthly precipitation at two National Oceanic and Atmospheric Administration climate stations near the Big River Basin, Missouri, October 2011–September 2013</li> <li>Graph showing daily mean streamflow computed during the study period at two study sites on the Big River, Missouri, October 2011–September 2013</li> <li>Graph showing daily mean streamflow computed during the study period at two study sites on the Big River, Missouri, October 2011–September 2013</li> </ol>	11
<ol> <li>Graph showing total monthly precipitation at two National Oceanic and Atmospheric Administration climate stations near the Big River Basin, Missouri, October 2011–September 2013</li> <li>Graph showing daily mean streamflow computed during the study period at two study sites on the Big River, Missouri, October 2011–September 2013</li> <li>Graphs showing daily mean water temperature measured at two study sites on the</li> </ol>	12
<ol> <li>Graph showing daily mean streamflow computed during the study period at two study sites on the Big River, Missouri, October 2011–September 2013</li> <li>Graphs showing daily mean water temperature measured at two study sites on the</li> </ol>	14
7. Graphs showing daily mean water temperature measured at two study sites on the	15
Big River, Missouri, October 2011–September 2013	17

8.	Graphs showing daily mean turbidity measured at two study sites on the Big River, Missouri, October 2011–September 2013	18
9.	Graphs showing continuous streamflow and discrete suspended-sediment concentration samples collected at two study sites on the Big River, Missouri, October 2011–September 2013	19
10.	Graphs showing daily mean suspended-sediment concentrations computed at two study sites on the Big River, Missouri, October 2011–September 2013	22
11.	Graphs showing daily mean suspended-sediment loads computed at two study sites on the Big River, Missouri, October 2011–September 2013	23
12.	Graphs showing trace-element concentrations in two suspended-sediment size fractions collected during stormflow events at two study sites on the Big River, Missouri, October 2011–September 2013	28
13.	Graphs showing seasonal comparison of stormflow-event suspended-sediment concentrations and mass-accumulation lead and zinc concentrations within suspended sediments for two study sites on the Big River, Missouri, October 2011–September 2013	31
14.	Graphs showing seasonal comparison of stormflow-event loads and yields of lead and zinc in suspended sediments at two study sites on the Big River, Missouri, October 2011–September 2013	35

# Tables

1.	Location information for study sites on the Big River, Missouri	5
2.	Reporting limits of laboratory analyses	8
3.	Summary statistics of model-calibration datasets for two study sites on the Big River, October 2011–September 2013	10
4.	Streamflow statistics for two study sites on the Big River, Missouri, October 2011–September 2013	15
5.	Water-quality statistics for two study sites on the Big River, Missouri, October 2011–September 2013	16
6.	Concentrations and size distributions of suspended-sediment samples collected at two study sites on the Big River, Missouri, October 2011–September 2013	20
7.	Daily suspended-sediment concentration and load statistics at two study sites on the Big River, Missouri, October 2011–September 2013	24
8.	Suspended-sediment concentrations, loads, and yields from sampled stormflow events at two study sites on the Big River, Missouri, October 2011–September 2013 .	25
9.	Selected trace-element concentrations for two particle size distributions of suspended sediments collected during stormflow events at two study sites on the Big River, Missouri, October 2011–September 2013	26
10.	Streamflow, suspended-sediment concentrations and particle-size distributions, and selected total trace-element concentrations in suspended sediments collected during stormflow events at two study sites on the Big River, Missouri, October 2011–September 2013	30
11.	Selected trace element concentrations, loads, and yields in suspended sediments from sampled stormflow events at two study sites on the Big River, Missouri, October 2011–September 2013	32

# **Conversion Factors**

[Inch/Pound to International System of Units]

Multiply	Ву	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	4,047	square meter (m <sup>2</sup> )
square foot (ft <sup>2</sup> )	929.0	square centimeter (cm <sup>2</sup> )
square foot (ft <sup>2</sup> )	0.09290	square meter (m <sup>2</sup> )
square inch (in <sup>2</sup> )	6.452	square centimeter (cm <sup>2</sup> )
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )
	Volume	
cubic foot (ft <sup>3</sup> )	0.02832	cubic meter (m <sup>3</sup> )
gallon (gal)	3.785	liter (L)
	Flow rate	
foot per second (ft/s)	0.3048	meter per second (m/s)
cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second (m <sup>3</sup> /s)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	metric ton (t)
ton per day (ton/d)	0.9072	metric ton per day
ton per day (ton/d)	0.9072	megagram per day (Mg/d)
short ton per day per square mile	0.3503	megagram per day per square kilometer [(Mg/d)/km²]
ton per year (ton/yr)	0.9072	megagram per year (Mg/yr)
ton per year (ton/yr)	0.9072	metric ton per year

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  $^{\circ}F=(1.8\times^{\circ}C)+32$ 

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:  $^{\circ}C=(^{\circ}F-32)/1.8$ 

# Datum

Vertical coordinate information is referenced to North American Vertical Datum of 1988 (NAVD 88).

# **Supplemental Information**

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ( $\mu$ g/L).

Concentrations of chemical constituents in sediments are given in milligrams per kilogram (mg/kg).

Water year in U.S. Geological Survey reports is the 12-month period October 1 through September 30. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 2013 is called the "2013 water year."

## **Abbreviations**

ADAPS	automated data processing system
ADCP	acoustic Doppler current profiler
ASTM	Association of Standards and Testing Materials
CWOM	continuous water-quality monitor
DCP	data collection platform
EPA	U.S. Environmental Protection Agency
EWI	equal-width increment
FISP	Federal Interagency Sedimentation Project
FNU	formazin nephelometric units
ICP-MS	inductively-coupled plasma mass-spectrometry
MDNR	Missouri Department of Natural Resources
MRL	Minerals Research Laboratory
NIST	National Institute of Standards and Technology
NOAA	National Oceanographic and Atmospheric Association
NWIS	National Water Information System
PEC	probable effect concentration
PVC	polyvinyl chloride
<i>R</i> <sup>2</sup>	coefficient of determination
$R^2_a$	adjusted coefficient of determination
SQG	sediment quality guidelines
SSC	suspended-sediment concentration
SSL	suspended-sediment load
TEC	threshold effect concentration
TET	toxic effect threshold
USFWS	U.S. Fish and Wildlife Service
USGS	U.S. Geological Survey
YSI	Yellow Springs, Incorporated

By Miya N. Barr

## Abstract

Missouri was the leading producer of lead in the United States—as well as the world—for more than a century. One of the lead sources is known as the Old Lead Belt, located in southeast Missouri. The primary ore mineral in the region is galena, which can be found both in surface deposits and underground as deep as 200 feet. More than 8.5 million tons of lead were produced from the Old Lead Belt before operations ceased in 1972. Although active lead mining has ended, the effects of mining activities still remain in the form of large mine waste piles on the landscape typically near tributaries and the main stem of the Big River, which drains the Old Lead Belt. Six large mine waste piles encompassing more than 2,800 acres, exist within the Big River Basin. These six mine waste piles have been an available source of trace element-rich suspended sediments transported by natural erosional processes downstream into the Big River.

A study was performed by the U.S. Geological Survey in cooperation with U.S. Environmental Protection Agency, Region 7, to calculate and characterize suspended-sediment quantity and quality within the Big River basin after reclamation of the mine waste piles ended in 2012. Streamflow and suspended sediments were quantified and sampled at two locations along a 68-mile reach of the Big River between Bonne Terre and Byrnes Mill, Missouri. The results will help regulatory agencies, such as the U.S. Environmental Protection Agency and U.S. Fish and Wildlife Service, determine impaired reaches and ecosystems for remedial and restoration efforts.

Continuous stream stage, water temperature, and turbidity, and discrete suspended-sediment concentration data were collected at the two sites between October 2011 and September 2013. Suspended-sediment samples were collected during various hydrologic conditions to develop a regression model between discrete suspended-sediment concentration and continuous turbidity. Suspended sediments collected during stormflow events were analyzed for concentrations of trace elements such as barium, cadmium, lead, and zinc within two sediment size fractions. Event loads and annual loads of suspended sediment and select trace elements in suspended sediments also were calculated. Suspended-sediment loads computed by the regression model increased downstream from about 201,000 tons at the upstream site to about 355,000 tons at the downstream site during the study period. Stormflow-event-based (hereinafter referred to as "event-based") suspended-sediment loads ranged from 180 to 32,000 tons at the upstream sampling site and 390 to 53,000 tons at the downstream site along the Big River. Although only seven stormflow events at the upstream site and six at the downstream site were sampled, the event-based suspended-sediment loads accounted for nearly 30 percent of the total suspended-sediment loads computed at both sites, indicating most of the suspended sediment transported through the Big River occurs during higher streamflows.

Sediment quality guidelines, known as the threshold effect concentration and the probable effect concentration, used to assess toxicity of trace-element concentrations in sediments were compared to the cadmium, lead, and zinc concentrations in suspended sediment samples collected during stormflow events. All concentrations of cadmium, lead, and zinc in event-based suspended sediment samples exceeded the threshold and probable effect concentrations. Lead and zinc concentrations in the sediment size fraction less than 0.063 millimeters also exceeded the toxic effect threshold, above which sediment is considered to be heavily polluted causing adverse effects on sediment-dwelling organisms. Concentrations of cadmium and zinc in event-based suspended sediment samples were notably higher in samples from the upstream site than samples from the downstream site, indicating the sources of sediments enriched in these trace elements decrease in the downstream area of the watershed. The reduction in concentration of cadmium and zinc could be from dissolution of the constituents during transport or possibly a decrease in downstream source material. The lead concentration exceedance of the probable effects concentration as well as the threshold effects concentration indicates that lead-rich suspended sediments in the fraction less than 0.063 millimeters are readily available within the Big River Basin for transport. These sediments remain in the system from historical mining, and as the reclamation of mine waste piles in the upstream area of the watershed reduce additional sediment loadings, these fine sediments may be continually

released as the river scours the streambed and erodes stream banks causing the lead-rich suspended sediment to remain in a state of equilibrium.

Barium concentrations in suspended-sediments were nearly twice as high in stormflow event samples collected at the downstream site as compared to samples from the upstream site. The source of barium in the Big River could be from Mineral Fork and Mill Creek, which flow through the historical barite (barium sulfate, also known as tiff) mining district in Washington County, and discharge into the Big River between the two study sites.

Total trace-element loads and yields in suspended sediments were computed from the sampled events for each year in the study. The total barium loads in suspended sediments were higher for sampled events collected at the downstream site than the upstream site during both study years. Cadmium and zinc loads in suspended sediments were lower at the downstream site than the upstream site, although the decrease in total load was not substantial during the study period. Lead loads in suspended sediments were lower at the downstream site during the first study year, with a slightly higher load downstream in the second year though the increase from upstream to downstream was small. Event-based yields were higher at the upstream site, indicating that readily available sediment sources are closer to the upstream site where more mining affected areas are located. The estimates determined during large precipitation events indicate that large sources of suspended sediments with large concentrations of trace elements are still available for transport within the Big River.

## Introduction

Missouri was the leading producer of lead in the world for more than a century (Missouri Department of Natural Resources, 2014). An important source of lead was the Old Lead Belt, a sub district of the Southeast Missouri Lead District, located primarily in St. Francois County in southeastern Missouri (fig. 1). Galena was the primary ore mineral and could be found on surface outcrops and as deposits that extended nearly 200 feet vertically and thousands of feet laterally. Lead mining began in southeastern Missouri in the early 1700s, at which time mines were mostly shallow pits operated by French explorers, and continued as individual small operations until the mid-1860s (Missouri Department of Natural Resources, 2014). In 1864, the St. Joseph Lead Company acquired 964 acres and began mining at Bonne Terre, Missouri (fig. 1). With the implementation of diamond-bit core drilling, lead deposits deep beneath the surface were discovered under much of the Big River Basin. Fifteen companies had mining operations in the Old Lead Belt by the early 1900s. Mining operations were gradually shut down during the late 1950s and early 1960s as ore deposits were depleted and mining in other parts of the State was more productive. More than 8.5 million tons of lead were produced from the Old Lead Belt before the

St. Joseph Lead Company closed operations in 1972 (Missouri Department of Natural Resources, 2014). Although active lead mining ended more than 40 years ago, the effects of mining still remain within the region in the form of mining waste (tailings and chat) piles on the land surface. These piles are generally located near tributaries and the main stem of the Big River and are readily available sources of lead-rich suspended sediments that can enter into the watershed during runoff and by wind transport.

The Big River is the main riverine system that drains the Old Lead Belt. The Big River runs generally south to north and is 145 miles in length from its source to the confluence with the Meramec River (fig. 1). Data collection during previous U.S. Geological Survey (USGS) investigations, in cooperation with Missouri Department of Natural Resources (MDNR), indicated that streambed sediments collected in the Meramec River downstream from the Big River have higher lead concentrations than those collected upstream from the Big River confluence (U.S. Geological Survey, 2015). These results indicate that lead-rich suspended sediments have been transported from the Big River in the past, but limited information is currently (2015) available to determine the amount of suspended sediments associated with mining wastes that are readily available for transport by the Big River through fluvial processes and whether these suspended sediments still contain mining-related metals. Additional information was needed to quantify daily sediment loads and the concentrations of lead and other metals of concern during stormflow events within the Big River Basin. Such information can assist regulatory agencies such as the U.S. Environmental Protection Agency (EPA) and the U.S. Fish and Wildlife Service (USFWS) in determining impaired reaches and ecosystems for remedial and restoration efforts. A study was performed by the U.S. Geological Survey in cooperation with U.S. Environmental Protection Agency, Region 7, to assess the amount and availability of suspended sediments within the Big River Basin after chat pile capping efforts ended in 2012 that completed a 4-year reclamation effort, and to assess the trace-element concentrations of suspended sediments transported through the basin.

## **Study Background**

Although mining activities are not currently (2015) being conducted in the Big River Basin, six large chat piles consisting of approximately 2,800 acres (Mosby and Weber, 2009) remain on the land surface upstream from the study reach that is located between two USGS streamgages (fig. 1). These large amounts of mine waste, sometimes spanning more than a mile in diameter, began with the introduction of industrial-grade mining and milling methods in the early 1900s. Materials excavated from below the land surface were crushed or ground using jig tables in the earlier periods, and after the 1920s chemical flotation techniques were used to separate lead from the host rock. The leftover host rock was discarded into chat (larger pieces from crushing) or tailings (smaller material from



Figure 1. Location of study sites and the Big River Basin.

the flotation process) piles. Neither method was completely effective at separating ore from host rock. Some operations would re-mill existing chat piles to recover lead missed from basic crushing methods (Missouri Department of Natural Resources, 2014). These piles have resulted in a source of suspended sediments available for transport by natural erosional processes such as storm event runoff and wind into the Big River. Between 2008 and 2012, the EPA conducted reclamation efforts to cap and prevent further erosion of the piles (Mosby and Weber, 2009).

Previous USGS studies have determined surface-water quality, and physical and chemical processes related to the quality of water, trace-element concentrations of suspendedsediment and streambed-sediment particles of various sizes, and loads of select trace elements in dissolved and solid phases (Smith and Schumacher, 1991, 1993); however, limited information is available on the current (2015) amount of suspended sediments transported through the Big River as well as the concentration of trace elements in suspended sediments. As capping efforts have been made to restrict additional sediment sources, it is important to determine the amount of suspended sediments that are still available for transport through the basin as well as to assess the effectiveness of the reclamation efforts over time.

Sediments are fragments of parent materials that have been affected by erosional processes and are transported by, suspended in, or deposited by water or air, and also can accumulate in beds (Edwards and Glysson, 1999). The USGS defines sediments transported by water as "fluvial sediments." Fluvial sediments are fragmented material derived from weathering of larger rocks and transported by, suspended in, or deposited by water, and can include biological and chemical precipitates and decomposed organic materials (Edwards and Glysson, 1999). Finer-grained fluvial sediments are transported in suspension because of the velocity and currents of the stream, whereas coarser sediments are transported closer to the streambed by rolling and skipping along the streambed. The finer, suspended particles tend to be transported at the same rate that the stream flows, whereas the coarser materials are only transported when the system experiences higher velocities and generally are at rest most of the time (Edwards and Glysson, 1999). The supply of finer materials in suspension (also known as the "wash load") usually has a greater effect on the suspended-sediment concentration (SSC) than streamflow conditions, because the rate of supply varies during and between events as well as from seasonal precipitation and vegetation (Charlton, 2008). Increases in streamflow produce increased SSC as erosion increases, releasing finer particles from storage. The computation of daily SSC and suspended-sediment load (SSL) is useful in various applications such as describing variability in suspended-sediment conditions, evaluating water-resource management practices and goals, predicting reservoir capacities, evaluating waterquality criteria, understanding stream channel morphology,

and comparing sediment characteristics between basins (Rasmussen and others, 2009).

Turbidity is a qualitative parameter defined by an optical measurement of scattered and absorbed light as it interacts with solid particles through a fluid sample, and measurements are expressed in units based on the technology used as well as the calibration standards (ASTM International, 2011). Suspended and dissolved organic and inorganic materials such as sediments (sands, silts, and clays), algae, microorganisms, organic acids, and dyes are common causes of turbidity in fluvial systems. Turbidity can assist with the computation of time-series SSC, monitoring land use and other human-related activities, and natural resource restoration (Anderson, 2005).

Trace element concentrations are related to sediments in streams by a number of factors including grain size, surface area, and sediment composition (Horowitz and Elrick, 1987). As the proportion of grain size increases, the trace element concentrations associated with the sediments also increase. The surface area of the grains also affects the concentration of trace elements as a larger surface area allows for stronger bonding, most commonly in sediment size fractions less than 0.063 millimeters (mm). When an abundance of very fine-grained sediments are present, the particles can attach together creating aggregates, which increase the mean grain size of a sample and reduces available surface area. The aggregates of sediments less than 0.063 mm can affect trace element concentrations in a sample more than larger size fractions of sands (Horowitz and Elrick, 1987).

### Purpose and Scope

The purpose of this report is to present the results of a hydrologic investigation to characterize and calculate suspended-sediment quantity and quality being transported through the lower Big River, Mo., based on data collected October 2011 through September 2013. The report describes the techniques and methods used to collect and analyze waterquality constituents such as water temperature and turbidity; suspended-sediment concentration, load, and particle-size distribution; and selected trace-element concentration load in sediments at two sites on the main stem of the Big River during stormflow events.

### **Description of Study Area**

The area of study is a 68-mile reach of the Big River, between the towns of Bonne Terre and Byrnes Mill, Mo. (fig. 1; table 1). Two sites were used in this study: Big River below Bonne Terre, Mo. (USGS site number 07017610; hereinafter referred to as the upstream site) and Big River at Byrnesville, Mo. (USGS site number 07018500; hereinafter referred to as the downstream site). The upstream site is located less than 5 miles downstream from the Old Lead Belt, and the downstream site is located about 68 miles downstream from Bonne Terre. The Big River discharges into the Meramec River, approximately 15 miles downstream from the downstream site. The Meramec River discharges into the Mississippi River south of St. Louis, Mo. The study area is located within the Salem Plateau of the Ozark Plateaus physiographic province (Fenneman, 1938). The topography of the upper reaches of the study area is rugged with narrow, steep drainage divides and several hundred feet of relief. The lower reaches also have some steep drainage that gradually transition to large flood plains. Land-surface altitudes range from about 400 to 1,000 feet (ft) above North American Vertical Datum of 1988 (NAVD 88). Stream width is generally 50 ft in the upper reaches of the basin and can span nearly 100 ft in the lower reaches. The streambed consists mainly of coarse materials such as cobbles, gravels, and sands in the upper reaches and smaller-grained particles such as sands and silts in the lower reaches. Land use in the Big River Basin is approximately 72 percent forest, 18 percent grassland, 7 percent urbanized or developed, and 1 percent cropland (Missouri Department of Natural Resources, 2013). Some low-head mill dams are still present, which can alter and control the streamflow. Tributaries along the Big River include Cedar Creek, Flat Creek, Mill Creek, and Mineral Fork. Mineral Fork, the largest tributary with a basin area of 189 square miles (mi2; Missouri Department of Natural Resources, 2013), discharges into the Big River between the two study sites. No streamflow-gaging station (hereinafter referred to as streamgage) is located on Mineral Fork or the other tributaries in the basin

## Methods

In order to quantify the transport of sediment and the concentration and flux of selected metals in the Big River, streamflow and suspended sediments were quantified and sampled at the two study sites. All field and laboratory methods described in this report were consistently performed at both sites during the study period. Any variations have been documented and described fully within this study report.

### Methods 5

### **Field Methods**

The upstream site was established for this study and began operation on October 13, 2011. The site is located at the bridge on County Highway E, approximately 3 miles north of Bonne Terre (fig 1; table 1). The drainage area of the upstream site is 409 mi<sup>2</sup>. The pressure transducer orifice line and continuous water-quality monitor (CWQM) are deployed from the left stream bank (facing downstream) under the highway bridge. During base-flow conditions, streamflow measurements and suspended-sediment samples were obtained approximately 40 ft upstream from the streamgage. Measurements and samples during high-flow conditions (hereinafter referred to as "event sampling") were collected from the bridge deck on Highway E. The stream channel at this site location is relatively shallow and narrow (2 to 3 ft deep and 60 ft or less wide) and the streambed consists of fine sands, gravels, large cobbles, and some boulders.

The downstream site has been an active streamgage from May 1922 to present (2015); is located on the left edge of the water on a privately owned bridge near Old Byrnesmill Road in Byrnesville, Mo.; and has a drainage area of 917 mi<sup>2</sup> (fig 1; table 1). The CWQM was deployed from the left side of the stream along a rock bluff just under the bridge, next to the orifice line. The streamgage is approximately 100 ft downstream from an old low-head mill dam. During base-flow conditions, streamflow measurements and suspended-sediment samples were obtained by wading approximately 300 ft downstream from the streamgage, which is downstream from the bridge on Old Byrnesmill Road. If wading conditions were not safe, measurements and samples were collected from the bridge on Old Byrnesmill Road, which was the location of all event sampling. The stream channel at the wading section is usually 3 to 5 ft deep and 80 to 100 ft wide, and the streambed consists primarily of gravels and coarse sands with some finer sands and silts.

Study sites were equipped with a data collection platform (DCP) that stored information from the non-submersible pressure transducer used for measuring stream stage and from

Table 1. Location information for study sites on the Big River, Missouri.

[USGS, U.S. Geological Survey; mi2, square miles; in., inches]

USGS site number (fig. 1)	Station name	Study location description	Latitude (degrees/ minutes/ seconds)	Longitude (degrees/ minutes/ seconds)	Drainage area (mi²)	County	Average monthly precipitation <sup>1</sup> (in.)	Period of stream- flow record used in this study
07017610	Big River below Bonne Terre, Missouri	upstream	37°57′55.9″	90°34′27.9″	409	St. Francois	3.6	October 2011– September 2013
07018500	Big River at Byrnesville, Missouri	downstream	38°23'30.2″	90°38'16.1″	917	Jefferson	3.2	May 1922– September 2013

<sup>1</sup>Average monthly precipitation was computed using only monthly precipitation data within the study period (October 2011 through September 2013).

the CWQM used to measure water temperature and turbidity. Stream stage, water temperature, and turbidity were recorded by the DCP every 15 minutes and transmitted hourly by way of satellite telemetry. All water-quality data were archived along with streamflow data in the USGS National Water Information System (NWIS; U.S. Geological Survey, 2015). The CWQMs were deployed using polyvinyl chloride (PVC) pipe. The PVC pipe had multiple 1-inch (in.) holes drilled to allow water from the stream to flow freely around the instrument, reducing bias in data from readings of stagnant water trapped in the pipe.

Instantaneous streamflow measurements were made every 4 to 6 weeks at the two sites and during event sampling to determine and maintain a stage-discharge relationship using standard USGS methods and techniques (Rantz and others, 1982; Sauer, 2002; Oberg and others, 2005; Turnipseed and Sauer, 2010; Mueller and others, 2013). Instantaneous measurements were made with various acoustic doppler current profilers (ADCP) by wading during low-flow conditions and from the bridge decks during high flows or if the wading sections could not be accessed safely.

Water temperature was recorded in degrees Celsius (°C) and turbidity was reported in formazin nephelometric units (FNU). Thermistors used for water temperature measurements were checked against a National Institute of Standards and Technology (NIST) calibrated thermometer and received at minimum a 3-point calibration check as documented in Wilde (2006). Many different sensors and models of turbidometers are available for field measurements. For this study, a YSI Incorporated sensor model 6136 (YSI 6136) was used to record instantaneous turbidity readings at both sites as well as the field meter to reduce any bias between sensor makes or models. The advantage of the YSI 6136 is that erroneous readings are reduced because the sensor is equipped with a wiper.

For the purpose of this study, only suspended sediments were collected. Suspended-sediment loads described in this study are considered to represent the majority of sediments transported in suspension within the Big River and are referred to as SSL. No bedload sampling was performed; therefore, any loads computed from the results are not intended to be considered a total sediment load.

Cross-sectional (discrete) suspended-sediment samples were collected during stormflow events and almost every month during base-flow conditions. Uses of the suspendedsediment samples were two-fold—to determine a relation with turbidity data to compute a daily SSC (that is, calibrate the regression model), and to measure trace-element concentrations of the suspended sediments being transported during a stormflow event. Stormflow events were defined in this study as a rapid and substantial change in streamflow and turbidity. The magnitude and duration of stormflow events varied and collection efforts were not always successful or possible.

The monthly suspended-sediment collections at base flow were collected by wading in the stream and using a depth-integrated and isokinetic (stream water approaching and entering the sampling nozzle have the same velocity) sampler known as a US DH-81 sampler. The US DH-81 contained a rigid, polyethylene 1-liter (L) sampling bottle and one-quarter in. Teflon<sup>®</sup> nozzle. The equal-width increment (EWI) sampling method was used to obtain the sediment sample as described in Wilde and others (2004). The sampler was raised and lowered at a consistent transit rate at each sampling interval (vertical). If multiple 1-L bottles were used to collect at all verticals, the bottles were composited by the laboratory for analysis. If the minimum mean stream velocity was less than 1.5 feet per second (ft/s), isokinetic conditions no longer existed, and baseflow samples were collected using grab sampling methods as described in Wilde and others (2004).

If stream conditions were not conducive to wading because of depth, debris, high velocities, or other conditions that made wading dangerous, suspended-sediment samples were collected from the bridge deck at each site. The samplers were attached to a reel and cable mechanism on either a 3-wheeled base or a crane structure mounted to the front of a field vehicle. The reel was hand-operated at a constant speed based on the transit rate computed by the maximum velocity and depth. A one-quarter in. nozzle was used to collect all particles classified as sand-sized and smaller. Collection was performed using the same EWI techniques used for base-flow sampling except with a heavier sampler to maintain isokinetic sampling requirements (Wilde and others, 2004). Depending on the average stream depth and velocities during stormflow events, either a US DH-95 or US DH-2 sampler was used. Descriptions of each sampler and the limitations of each are described in Wilde and others (2014). Samples were collected at multiple points along the hydrograph, including the rising limb, the event peak, and the falling limb, when possible. Streamflow measurements also were collected as close to the peak as possible. The suspended-sediment concentration samples along the hydrograph were analyzed individually to compute the concentration flux throughout the event. Samples to be analyzed for trace-element concentrations were collected using the clean hands/dirty hands techniques as described in U.S. Geological Survey (2006).

Samplers used by the USGS, as recommended by the Federal Interagency Sedimentation Project (FISP) for the collection of suspended sediments (Davis, 2005), cover a wide range of sampling capacities and conditions and have a limitation on the depth within the water column at which sampling can occur, based on the nozzle size and location in relation to the bottom of the sampler. The portion of depth near the streambed that cannot be reached by the nozzle is called the unsampled zone and can carry a higher concentration and coarser-sized sediment, which may or may not account for a large portion of the total suspended sediment, depending on stream velocity, depth, and turbulence through the sampled vertical (Edwards and Glysson, 1999). The concentration obtained within the measured depth is nearly equal to the concentration in the unsampled zone, as noted in Edwards and Glysson (1999), if the velocity and turbulence within the sampled depth are efficiently keeping sediments suspended within the total depth and are greater than the forces

transporting sediments along the streambed in the unsampled zone. The USGS samplers used in this study had unsampled zones of 4 in. for the DH-81 and DH-2 and 4.8 in. for the DH-95 (Davis, 2005; Wilde and others, 2014).

### Laboratory Methods

All suspended-sediment samples were processed at the USGS Missouri Water Science Center Sediment Laboratory in Rolla, Mo. Samples were delivered to the lab within 5 days of collection. Base-flow samples were analyzed for SSC in milligrams per liter using a filtration method as described in Guy (1969). All SSC results are available on NWISWeb at http://waterdata.usgs.gov/mo/nwis/qw.

Event samples were analyzed for SSC as well as particle size distribution of the sands (sediments greater than 0.063 mm) and fines (sediments less than 0.063 mm) fractions. Samples collected during events were sieved using techniques described in Guy (1969). Sieve mesh with openings of approximately 0.0625 mm and made of nylon fibers was used to reduce possible trace-element contamination from using traditional brass or stainless steel mesh sieves. All sediments in the sample were washed through the mesh sieve using deionized water. Fines which passed through the sieve were captured in a glass dish. All sediments remaining on the sieve mesh were rinsed into a separate glass dish, then both fractions were dried at 80 °C until all visible water was evaporated, followed by additional drying at 103 °C for one hour (Guy, 1969). If the mass for either sieved fraction was greater than or equal to 0.25 grams (g), the fraction could be analyzed for trace-element concentrations at the USGS Minerals Research Laboratory (MRL) in Denver, Colorado.

Dried fractions for trace-element analyses were shipped to the USGS MRL in glass vials. A suite of 42 trace elements was measured by inductively-coupled plasma mass-spectrometry (ICP-MS) using an acid digestion using documented laboratory methods (Taggart, 2002). Trace elements analyzed for this study as well as sediment analyses and the reporting limits are listed in table 2. All trace-element concentrations for each size fraction were stored in NWIS and are available at http://waterdata.usgs.gov/mo/nwis/qw.

### Quality Assurance and Quality Control

Quality assurance consists of techniques and practices used within a study to meet defined levels of quality with a known level of confidence to ensure the most accurate data possible. Such practices begin with site and equipment selection, sampling and maintenance frequencies and methods, personnel training and safety, and laboratory selection, all of which ensure the goals of the study are met. A USGS internal quality-assurance plan, summarized in this section, was created and used to document techniques and methods specific to the study with USGS guidelines. Data transmissions to NWISWeb were reviewed daily to remove erroneous data quickly and efficiently from the sensor record. Documentation of service visits and the calibration of the CWQM were archived and describe actions taken during the visit. Sediment sampling documentation also was archived and describes sampling conditions, sample type, sampling methods, equipment used, and other information as needed. Laboratory analysis request forms were used for both the sediment lab and the USGS MRL to document and track the samples and the analyses.

Data transmitted from the DCP at each site were reviewed daily for consistency and for determining the need for event sampling. CWQMs were serviced and calibrated following USGS guidelines as described in Wagner and others (2006). Construction setup and monitor selection was determined during reconnaissance before the start of the project to reduce effects of fouling, low-flow conditions, and damage from flooding or vandalism, and to guarantee safety in accessing the equipment. CWQMs were serviced on at least a monthly schedule and additionally when the data appeared erratic or anomalous. The monitors were cleaned, inspected for damage, and checked for calibration drift. If the calibration drift was greater than USGS criteria, the sensors were recalibrated. If the fouling or calibration drift was greater than USGS criteria as stated in Wagner and others (2006), the data were removed from the record.

Efforts were made to minimize contamination from sampling equipment, surrounding structures, and vehicles during event sampling. The clean hands/dirty hands technique as described in U.S. Geological Survey (2006) was used throughout the sampling procedures at a site. Containers for sample compositing were kept sealed and protected in a large plastic bag to prevent contamination by airborne debris caused by wind, vehicle traffic, the sampling crane, bridge railings, and precipitation.

Quality-control samples help identify and quantify bias and variability in sampling techniques such as sampling equipment, processing, shipping, and handling of the sample (U.S. Geological Survey, 2006). During the study, qualitycontrol samples were collected in the form of replicate suspended-sediment samples and laboratory blanks. A sequential replicate sample (collected in the same order after the environmental sample and composited into a second container) was performed when possible. Blank samples using deionized water processed by the USGS Missouri Water Science Center Sediment Laboratory were randomly assigned to sample shipments during the login phase for internal laboratory validation and quality assurance. USGS Sediment Laboratories participate in bi-annual quality-assurance tests to document inconsistencies within each lab and among all USGS labs for consistency in reporting results. Quality-assurance test results for the USGS Missouri Water Science Center Sediment Laboratory are available at the USGS Branch of Quality Systems at http:// bqs.usgs.gov/SLQA/. The USGS MRL created laboratory split replicates for 10 percent of a shipment to validate laboratory results for internal quality assurance and are available upon request from the USGS MRL at http://minerals.cr.usgs.gov/.

### Table 2. Reporting limits of laboratory analyses.

[%, percent; USGS SMRL, U.S. Geological Survey Minerals Research Laboratory; mg/L, milligrams per liter; mm, millimeters; USGS SDMO, U.S. Geological Survey Missouri Sediment Laboratory; --, not available]

Constituent	Reporting limit	Analyzing laboratory	Analytical reference
Aluminum, Al	0.01%	USGS SMRL	Taggart, 2002
Calcium, Ca	0.01%	USGS SMRL	Taggart, 2002
Iron, Fe	0.01%	USGS SMRL	Taggart, 2002
Potassium, K	0.01%	USGS SMRL	Taggart, 2002
Magnesium, Mg	0.01%	USGS SMRL	Taggart, 2002
Sodium, Na	0.01%	USGS SMRL	Taggart, 2002
Phosphorous, P	50 mg/L	USGS SMRL	Taggart, 2002
Titanium, Ti	0.01%	USGS SMRL	Taggart, 2002
Silver, Ag	1 mg/L	USGS SMRL	Taggart, 2002
Arsenic, As	1 mg/L	USGS SMRL	Taggart, 2002
Barium, Ba	5 mg/L	USGS SMRL	Taggart, 2002
Beryllium, Be	0.1 mg/L	USGS SMRL	Taggart, 2002
Bismuth, Bi	0.04 mg/L	USGS SMRL	Taggart, 2002
Cadmium, Cd	0.1 mg/L	USGS SMRL	Taggart, 2002
Cerium, Ce	0.05 mg/L	USGS SMRL	Taggart, 2002
Cobalt, Co	0.1 mg/L	USGS SMRL	Taggart, 2002
Chromium, Cr	1 mg/L	USGS SMRL	Taggart, 2002
Cesium, Cs	0.05 mg/L	USGS SMRL	Taggart, 2002
Copper, Cu	0.5 mg/L	USGS SMRL	Taggart, 2002
Gallium, Ga	0.05 mg/L	USGS SMRL	Taggart, 2002
Indium, In	0.02 mg/L	USGS SMRL	Taggart, 2002
Lanthanum, La	0.5 mg/L	USGS SMRL	Taggart, 2002
Lithium, Li	1 mg/L	USGS SMRL	Taggart, 2002
Manganese, Mn	5 mg/L	USGS SMRL	Taggart, 2002
Molybdenum, Mo	0.05 mg/L	USGS SMRL	Taggart, 2002
Niobium, Nb	0.1 mg/L	USGS SMRL	Taggart, 2002
Nickel, Ni	0.5 mg/L	USGS SMRL	Taggart, 2002
Lead, Pb	0.5 mg/L	USGS SMRL	Taggart, 2002
Rubidium, Rb	0.2 mg/L	USGS SMRL	Taggart, 2002
Sulfur, S	0.01%	USGS SMRL	Taggart, 2002
Antimony, Sb	0.05 mg/L	USGS SMRL	Taggart, 2002
Scandium, Sc	0.1 mg/L	USGS SMRL	Taggart, 2002
Tin, Sn	0.1 mg/L	USGS SMRL	Taggart, 2002
Strontium, Sr	0.5 mg/L	USGS SMRL	Taggart, 2002
Tellurium, Te	0.1 mg/L	USGS SMRL	Taggart, 2002
Thallium, Tl	0.1 mg/L	USGS SMRL	Taggart, 2002
Thorium, Th	0.2 mg/L	USGS SMRL	Taggart, 2002
Uranium, U	0.1 mg/L	USGS SMRL	Taggart, 2002
Vanadium, V	1.0 mg/L	USGS SMRL	Taggart, 2002
Tungsten, W	0.1 mg/L	USGS SMRL	Taggart, 2002
Yttrium, Y	0.1 mg/L	USGS SMRL	Taggart, 2002
Zinc, Zn	1 mg/L	USGS SMRL	Taggart, 2002
Suspended-sediment concentration (SSC)	0.5 mg/L	USGS SDMO	Guy, 1969
Suspended sediment, percent finer than 0.063 mm	0%	USGS SDMO	Guy, 1969

### **Data Analysis and Reporting**

Streamflow and water-quality constituent statistics were derived from daily mean, monthly mean, or annual mean values. The mean values were derived from the 15-minute data. Annual runoff was derived by dividing the annual mean streamflow in cubic feet per second by the drainage area in square miles, then multiplying by a conversion factor of 13.5744 to obtain the result in inches per water year. Monthly precipitation accumulations were obtained for weather stations near the study sites from the National Oceanographic and Atmospheric Administration (NOAA) and are cumulative precipitation measurements converted from millimeters to inches for consistency of units within the report.

Daily values of continuous water temperature and turbidity were published in the "Annual Water Year Summary Reports," which can be accessed through NWISWeb, along with other daily, monthly, and annual statistics (U.S. Geological Survey, 2015). Periods of missing data occurred because of extreme biological fouling such as algae and macroinvertebrates, siltation after large events, or extreme low-flow conditions. Turbidity values were used in a regression model for the computation of daily SSC. Because the magnitude of turbidity in fluvial systems is usually proportional to SSC (Rasmussen and others, 2009), continuous turbidity measurements also could be used to determine if a stormflow event was large enough to transport the minimum amount of suspended sediments required for the sediment chemistry analyses at the USGS MRL (0.25 grams).

A regression model for the computation of time-series SSC and SSL values was developed for each site using a dataset of discrete SSC and corresponding time-series turbidity and (or) streamflow. The dataset was used to calibrate the model and identify outliers and trends. Outliers were reviewed for erroneous entries, sampling method problems, or laboratory errors. For robust model development, the number of data pairs as well as the distribution of data over observed

Big River below Bonne Terre, Missouri

hydrologic conditions during the study is important (Rasmussen and others, 2009). The monthly base-flow sampling in combination with the multiple event values over a range of streamflows and turbidity measurements allowed for greater confidence in the model development for each site. Duration curves (fig. 2) show turbidity measurements at both sites were within the limits of the maximum level of accuracy (1,000 FNU) of the sensor model for all days in the study period except one.

During the 2012 water year (a water year is defined as a 12-month period beginning October 1 and ending September 30, designated by the calendar year in which it ends), 27 discrete SSC samples were collected and available for the model development at the upstream site. Non-transformed values of SSC were plotted against turbidity to determine if a statistically strong relationship existed (Rasmussen and others, 2009). Four outliers were detected by graphical inspection of the raw data and residual plots. The outliers occurred during storm events: two event SSC results collected on April 16, 2012; one sample on April 17, 2012; and one sample on September 8, 2012. The instantaneous turbidity values likely were biased from extreme fouling during the events rather than sediment sampling errors because when the CWQM could be accessed safely afterwards, the guard and deployment pipe were noted to be filled with gravel and mud. The four outliers were removed from the dataset. The remaining 23 data pairs were then plotted on a log-log scale to determine the strongest statistical relationship. The best-fit relation was determined to be from the power function, having an adjusted coefficient of determination  $(R^2)$  value of 0.92 and a level of significance (p-value) of 0.0043. During the 2013 water year, 13 discrete SSC results were added to the 2012 dataset to continue the regression model for the entire study period. No outliers were found in the 2013 water year dataset. The total dataset used in the study model for the upstream site included 36 pairs of data (table 3; fig. 3).



Figure 2. Turbidity duration curves for two study sites on the Big River, Missouri, October 2011–September 2013.

# Big River at Byrnesville, Missouri (07018500: downstream site)

Table 3. Summary statistics of model-calibration datasets for two study sites on the Big River, October 2011–September 2013.

[FNU, formazin nephelometric units; mg/L, milligrams per liter; ft<sup>3</sup>/s, cubic feet per second; --, not applicable]

Statistical summary of datasets							
	Tublic	Model data	set	Time-series dataset (17,240 hourly values)			
Summary statistic	(FNU)	Suspended-sediment concentration (mg/L)	Streamflow (ft³/s)	Turbidity (FNU)	Streamflow (ft³/s)		
Big River below Bonne Terre, Missouri (07017610; upstream site)							
Minimum	1.2	1	16	1	7.2		
Maximum	840	1,090	18,600	880	21,900		
Mean	117	170	2,840	15	450		
Median	46	74	637	6.2	130		
Standard deviation	196	230	5,530	44	1,510		
Number of unavailable turbidity values	1			2,214			
Number of data used in model	36	36					
	Big River at B	Syrnesville, Missouri (0701	8500; downstrear	n site)			
Minimum	3.1	4	61	0	51		
Maximum	790	870	24,600	715	28,280		
Mean	65	130	2,023	13	920		
Median	8.7	21	410	6.6	340		
Standard deviation	160	235	4,939	29	2,430		
Number of unavailable turbidity values	0			1,139			
Number of data used in model	25	25					

The final regression model for the upstream site, Big River below Bonne Terre (USGS Identifier 07017610), for the study period is as follows:

$$SSC = 1.8239(Turb)^{0.984}$$
 (1)

where

SSC	is suspended-sediment concentration, in
	milligrams per liter; and
Turb	is turbidity, in formazin nephelometric units
	measured with a YSI model 6136.

The model information used to develop equation 1 is as follows:

- Number of measurements = 36
- Residual standard error = 0.239
- Degrees of freedom = 33
- Adjusted coefficient of determination  $(R^2) = 0.92$

The downstream site had 19 SSC samples available for the development of the 2012 water year model. As was determined upstream, the SSC and turbidity data plotted in log-log scale made the best-fit relation at the downstream site using the power function, with an  $R_a^2$  value of 0.89 and a p-value of 0.0198. During model evaluation, three outliers were detected within the 2012 dataset-a routine base-flow collection on November 10, 2011; an event collection on March 17, 2012; and a routine base-flow collection on April 4, 2012. The SSC result for the November sampling date seemed to be biased high in relation to the turbidity results. The SSC sampling process may have inadvertently struck the sandy streambed, creating a re-suspension of bed materials. The March sample was during an event and could have been biased high during SSC collection or a possible turbidity sensor issue. The April outlier could have been because of a low-biased SSC collection (sampling rate too fast for the velocity) or erroneous turbidity readings. These three data points did not fit the general trend of the remaining points and were therefore removed from the dataset.

Paired SSC and instantaneous turbidity data collected at the downstream site during water year 2013 were added to the 2012 dataset to continue the regression model for the entire study period. Twelve data points were available from 2013; however, during model calibration and evaluation, three outliers were detected: January 31, 2013; April 20, 2013; and May 28, 2013. The January and April sampling dates had reasonable SSC results but because of extreme flooding and fouling of the turbidity sensor, no turbidity data were available



n = 25 n = number of datasets

**Figure 3.** Instantaneous turbidity in relation to discrete suspended-sediment concentrations used to develop a regression model for the computation of daily suspended-sediment concentrations and loads for two study sites on the Big River, October 2011–September 2013.

for comparison. The May sample had erroneous turbidity data because of extreme biofouling around the deployment pipe, and data were removed from the record. The total dataset used in the study model for the downstream site included 25 pairs of data (table 3; fig. 3). The model calibration remained statistically strong with the dataset of the full study period (seven outliers still removed), using the non-transformed SSC and turbidity data. The final regression model for the downstream site, Big River at Byrnesville (USGS Identifier 07018500) for the study period is as follows:

$$SSC = 1.786(Turb)^{1.050}$$
 (2)

where

SSC	is suspended-sediment concentration, in
	milligrams per liter; and
Turb	is turbidity, in formazin nephelometric units,
	measured with a YSI model 6136.

The model information used to develop equation 1 is as follows:

- Number of measurements = 25
- Residual standard error = 0.236
- Degrees of freedom = 23
- Adjusted coefficient of determination  $(R^2_{a}) = 0.89$

The regressions were applied to each instantaneous turbidity measurement available during the study period to compute time-series SSCs. The instantaneous turbidity measurements were stored in the NWIS subsystem ADAPS (automated data processing system), where mean daily SSC values also were computed and archived. The mean daily SSC values were then used to compute daily SSL values, also archived in ADAPS.

If no turbidity data were available or if the turbidity data were deemed unusable for sediment computation, a daily mean SSC value was computed using streamflow. The relationship was determined using similar techniques as SSCturbidity relationship analyses. Daily SSC results from the SSC-turbidity relationship were plotted against daily streamflow for the period of record available. Data were transformed until a best-fit relationship was determined. A best fit for both sites during the study was determined by plotting SSC and daily streamflow on a log-log scale (fig. 4). The SSCstreamflow relationship was not as statistically accurate as the SSC-turbidity relationship, and all daily SSC values computed using streamflow were flagged as estimated. SSL values computed from estimated SSC data also were flagged as estimated. The estimated daily SSC equation for the upstream site, Big River below Bonne Terre (USGS identifier 07017610), is as follows:

 $SSC = 0.3341(Q)^{0.8148}$  (3)

where

- SSC is suspended-sediment concentration, in milligrams per liter; and
  - *Q* is daily mean streamflow, in cubic feet per second.

The estimated daily SSC equation for the downstream site, Big River at Byrnesville (USGS identifier 07018500) is as follows:

$$SSC = 0.1668(Q)^{0.8469}$$
 (4)

where

SSC is suspended-sediment concentration, in milligrams per liter; and

*Q* is daily mean streamflow, in cubic feet per second.





Event-based SSLs were computed using the event-average SSC and the sampled runoff volume. The average SSC was the arithmetic average determined from all samples collected during the event. In some cases, only one sample could be collected because of timing of arrival, equipment issues, magnitude of event and rapid rises, and other various reasons. The sample runoff volume was the sum of the incremental streamflow in 15-minute intervals within the designated event duration divided by the event duration time. Using the streamflow data, the beginning and ending of each event was determined based on each event's increase or decrease in streamflow over time. The beginning of the event was established at the 15-minute streamflow value recorded one hour before the change in streamflow doubled. The end of the event varied by site and event because each event was unique in hydrologic conditions, but was determined when the streamflow was decreasing at a constant rate of 20 cubic feet per second ( $ft^3/s$ ) during each 15-minute measurement for at least 2 hours. The time between the established start and ending of the event was considered the event duration in hours. Event-based SSL was computed using the following equation:

$$ESSL = EMSSC \ge RV \ge (6.245 \ge 10^{-5})$$
 (5)

where

6

ESSL	is event-based suspended-sediment load, in
	pounds;
EMSSC	is event-based suspended-sediment
	concentration, in milligrams per liter;
RV	is runoff volume, in cubic feet; and
.245 x 10 <sup>-5</sup>	is a conversion from milligrams per liter to
	pounds per cubic foot.

Sediment yield is the amount of material removed from the land surface by erosion in a given unit of time per unit area of the hydrologic basin. Sediment yield is a useful tool for comparing study sites because it removes variation in basin size and event duration by normalizing the SSL. Event-based yields were computed for this study using the following equation:

$$EYield = ESSL/(DA \times ED)$$
(6)

where

EYield	is event-based suspended-sediment yield, in
	pounds per square mile per hour;
ESSL	is event-based suspended-sediment load, in
	pounds;
DA	is drainage area, in square miles; and
ED	is event duration, in hours.

Concentrations of barium, cadmium, lead, and zinc measured in suspended-sediment samples collected during events were used to compute event-based loads and yields of these constituents. In order to properly compute the traceelement concentration within the suspended sediments, a mass accumulation was computed using the constituent measurements from both size fractions. The equation used for the mass-accumulation computation of the total trace-element concentration in suspended sediment collected during events is as follows:

$$Conc_{total} = [(Conc_{s} \times (\%_{s}/100) + (Conc_{F} \times (\%_{F}/100))] \quad (7)$$
  
 
$$\times SSC/100,000$$

where

Conc <sub>total</sub>	is the total trace-element concentration in suspended sediments, in milligrams per liter;
<i>Conc</i> <sub>s</sub>	is the trace-element concentration in the sand fraction, in milligrams per kilogram;
% <sub>S</sub>	is the percent of mass in total sample considered sand (particles greater than 0.063 millimeters);
$Conc_{F}$	is the trace-element concentration in the fines fraction, in milligrams per kilogram;
% <sub>F</sub>	is the percent of mass in total sample considered fines (particles less than 0.063 millimeters);
SSC	is suspended-sediment concentration of total sample, in milligrams per liter; and
100,000	is the conversion factor from milligrams per

kilogram to milligrams per liter.

The mass accumulation computation used the sum of mass in each size fraction adjusted by the total SSC of the sample, then converted the trace-element concentration to milligrams per liter. When only one size fraction had enough mass for analyses, the trace-element concentration of the sample was still adjusted by the SSC, but should be assumed lower than the trace-element concentration that could be in the suspended sediments. An arithmetic average of trace-element concentrations were computed from all available suspendedsediment samples collected during the designated event duration. The event-based loads and yields were computed as previously described for the event-based suspended-sediment loads and yields in equations 5 and 6, using the arithmetic average of the trace element concentrations.

# **Surface-Water Quality**

Many ancillary conditions such as land use, topography, atmospheric conditions, and streamflow conditions such as extreme base flow (droughts) and stormflows (floods) can affect the overall quality of a stream. The assessment of these conditions were used to determine the surface-water quality of Big River and to compute loads and yields of suspended sediment and the loads and yields of trace elements in the suspended sediments.

### **Streamflow Conditions**

During the 2012 water year, Missouri's precipitation was less than normal at 34.67 in. compared to the long-term (approximately 100 years) State average of 41.03 in. (National Oceanic and Atmospheric Administration, 2013). In October 2011, about 40 percent of all Missouri counties had dry or drought conditions and about 60 percent were classified by the National Drought Mitigation Center (2013) as abnormally dry. From July through September 2012, all Missouri counties were experiencing at least moderate drought conditions. During August 2012, 35 percent of Missouri counties typically located in the northwest, southwest, and southeast corners of the State, were classified as having extreme drought conditions (National Drought Mitigation Center, University of Nebraska-Lincoln, 2013). Missouri's precipitation for the 2013 water year was 43.58 in., which is above the long-term State average (National Oceanic and Atmospheric Administration, 2014b).

Precipitation gages were not available at the study sites; therefore, monthly precipitation was obtained from two NOAA climate stations within the study area at DeSoto and Dittmer, Mo. (National Oceanographic and Atmospheric Administration, 2015; fig. 5). The DeSoto climate station is located in the southern part of the study area near the upstream site. The Dittmer climate station is located in the northern part of the study area near the downstream site. During the study period, monthly precipitation at both climate stations ranged from approximately 1 in. (at Dittmer in July 2012) to more than 7 in. (at DeSoto in April 2013). Monthly precipitation was consistent between the two climate stations for most of the 2012 water year with the exception of higher monthly precipitation amounts at the Dittmer station during May, August, and September 2012 and higher monthly precipitation at the DeSoto Station during November 2011. September 2012 had the highest monthly precipitation amounts for both climate stations during the 2012 water year. Monthly precipitation amounts increased during the 2013 water year, particularly from March through June, compared to the 2012 water year. Large differences in monthly precipitation between the climate stations were noted in January and July 2013, with the higher precipitation amounts recorded in the southern part of the study area at the DeSoto station. During the 2013 water year, April 2013 had the largest monthly precipitation amount recorded at the DeSoto station and March had the largest precipitation amount recorded at the Dittmer station.

The annual mean streamflow at the upstream site during the 2012 water year was approximately 189 ft<sup>3</sup>/s with an annual runoff of 6.27 in. (table 4). Annual mean streamflow and annual runoff during the 2013 water year was nearly four times higher than during the 2012 water year at 695 ft<sup>3</sup>/s and 23.06 in., respectively (table 4). At the downstream site, the annual mean streamflow during the 2012 water year was 419 ft<sup>3</sup>/s with an annual runoff of 6.22 in. The annual mean streamflow and annual runoff increased during the 2013 water year to 1,393 ft<sup>3</sup>/s and 20.63 in., respectively (table 4).

Streamflows were greatest in the spring months for the two study sites. At the upstream site, maximum daily streamflow was 2,390 ft<sup>3</sup>/s in March 2012 and 18,600 ft<sup>3</sup>/s in March 2013, and the minimum daily streamflow was 9.9 ft<sup>3</sup>/s in August 2012 and 42 ft<sup>3</sup>/s in September 2013 (table 4; fig. 6). Similar temporal variability also was measured at the downstream site. The maximum daily mean streamflow of 4,340 ft<sup>3</sup>/s was in March during water year 2012, and the maximum daily mean streamflow of 26,400 ft<sup>3</sup>/s was in April during the 2013 water year (table 4; fig. 6). The maximum peak streamflow during the study period was 21,900 ft<sup>3</sup>/s on April 19, 2013, at the upstream site, and the maximum peak streamflow during the study period was 28,700 ft<sup>3</sup>/s on April 20, 2013, at the downstream site. The historical maximum peak streamflow recorded at the downstream site was 63,600 ft<sup>3</sup>/s on September 25, 1993 (table 4).

### **Continuous Water Quality**

Water temperature is an important physical property because it can assist with quality control of monitor operations, such as detection of biological activity, extreme streamflow conditions, and human influences (Wilde, 2006). Water temperature is also a factor in determining a stream's physical fluid properties because viscosity is a factor in determining sediment transport efficiency (Charlton, 2008). The maximum water temperature recorded at the upstream site was 32.7 °C on July 25, 2012, and the minimum recorded water temperature was -0.1 °C on January 3, 2013 (table 5). At the downstream site, the maximum water temperature recorded water temperature was 0.5 °C on January 3, 2013 (table 5).



**Figure 5.** Total monthly precipitation at two National Oceanic and Atmospheric Administration climate stations near the Big River Basin, Missouri, October 2011–September 2013.

Table 4. Streamflow statistics for two study sites on the Big River, Missouri, October 2011–September 2013.

[ft<sup>3</sup>/s, cubic feet per second; ft, feet; in., inches]

Water year <sup>1</sup>	Maximum daily mean streamflow (ft³/s) and date		Minimum daily mean streamflow (ft <sup>3</sup> 's) and date		Maximum peak streamflow (ft³/s) and date		Maximum peak stage (ft) and date		Annual mean streamflow (ft³/s)	Annual runoff (in.)
		l	Big Rive	r below Bonne Te	erre, Misso	uri (07017610; ups	stream s	site)		
2012	2,390	March 17, 2012	9.9	August 11, 2012	4,810	March 16, 2012	11.98	March 16, 2012	<sup>2</sup> 189	<sup>2</sup> 6.27
2013	18,600	March 18, 2013	42	September 14, 2013	21,900	April 19, 2013	26.54	April 19, 2013	695	23.06
			Big Riv	er at Byrnesville,	Missouri (	07018500; downst	ream sit	te)		
2012	4,340	March 18, 2012	52	July 28, 2012	4,920	March 18, 2012	11.68	March 18, 2012	419	6.22
2013	26,400	April 20, 2013	115	September 15–17, 2013	28,700	April 20, 2013	23.58	April 20, 2013	1,393	20.63
1922–2013	57,800	September 25, 1993	25	August 30, 1936	63,600	September 25, 1993	29.37	September 25, 1993	863	12.90

<sup>1</sup>Water year is defined as the 12-month period beginning October 1 and ending September 30 of the calendar year in which it ends (water year 2012 is the period October 1, 2011 through September 30, 2012).

<sup>2</sup>Computed with incomplete data because the streamgage was not in operation until October 13, 2011.



**Figure 6.** Daily mean streamflow computed during the study period at two study sites on the Big River, Missouri, October 2011–September 2013.

Watar	Water temperature (degrees Celsius)										
year <sup>1</sup>	Maximum daily mean M and date		laily mean Minimum daily mean N Jate and date		Мах	Maximum recorded and date		Ainimum recorded and date			
Big River below Bonne Terre, Missouri (07017610; upstream site)											
2012	30.7	July 25, 2012	1.4	January 14, 2012	32.7	July 25, 2012	0.5	January 14, 2012			
2013	30.1	July 19, 2013	0.6	January 3, 2013	30.1	July 18, 2013	-0.1	January 3, 2013			
		В	ig River a	t Byrnesville, Missouri (07	018500; do	wnstream site)					
2012	30.0	August 8, 2012	1.5	January 14, 15, 2012	30.9	August 8, 2012	1.5	January 14, 15, 2012			
2013	30.1	July 19, 2013	0.7	January 3, 2013	30.7	July 19, 2013	0.5	January 3, 2013			

Table 5. Water-quality statistics for two study sites on the Big River, Missouri, October 2011–September 2013.

Watar		Turbidity (formazin nephelometric units)										
year <sup>1</sup>	Maximum daily mean N and date		Minimum daily mean Ma and date		aximum recorded and date		Minimum recorded and date					
Big River below Bonne Terre, Missouri (07017610; upstream site)												
2012	220	September 8, 2012	1.4	November 5, 2012	550	March 16, 2012	1	January 9, 10, 2012				
2013	520	March 18, 2013	1.5	November 21, 24, 2013	890	March 18, 2013	1.2	November 20-22, 2013				
		Bi	g River	at Byrnesville, Missouri (07	018500;	downstream site)						
2012	180	March 18, 2012	1.3	July 27, 2012	460	September 25, 2012	0.3	July 29, 2012				
2013	240	March 20, 2013	1.6	January 3–5, 7, 8, 2013	790	April 18, 2013	0	October 15, 2012				

<sup>1</sup>Water year is defined as the 12-month period beginning October 1 and ending September 30 of the calendar year in which it ends (water year 2012 is the period October 1, 2011 through September 30, 2012).

Water temperatures recorded at both sites followed similar diurnal variability and were similar at the two study sites. No water temperature data were corrected or missing for the upstream site during the study period. Water temperature data for the downstream site were unavailable from June 28 to July 30, 2012, because stream levels were too low for the temperature sensor to be submerged for proper measurements. Extreme flood debris, such as organic materials, large limbs and trees, and trash, affected the water temperature measurements during two events in water year 2013, causing data to be removed from April 19 through 24, and August 21 through 23, 2013 (fig. 7).

At the upstream site, daily mean turbidity ranged from 1.4 to 520 FNU during the study period (table 5; fig. 8). The maximum value recorded during the study was 890 FNU on March 18, 2013, and the minimum value was 1.0 FNU on January 9 and 10, 2012 (table 5). Missing daily values at the upstream site were commonly caused by extreme biofouling during warmer months with lower streamflows and siltation of the instrument and its deployment pipe during high flows. Efforts were made to service and eliminate such effects but were not always successful. Other factors were instrumentation malfunctions and drift between calibrations.

At the downstream site, turbidity measurements began on October 14, 2011. Daily mean turbidity ranged from 1.3 to 240 FNU for the study period (table 5; fig. 8). The maximum value recorded during the study was 790 FNU on April 18, 2013, and the minimum value recorded was 0 FNU on October 15, 2012 (table 5). No data were removed during water year 2012; however, during the 2013 water year, many days were removed because of siltation of the monitor and deployment pipe during higher streamflows. It was noted during the 2013 water year that a large amount of trees and vegetation were removed and some construction on the property adjacent to the monitor deployment pipe had occurred. These events may have increased the monitor fouling issues during storm events because exposed soil was readily available during runoff from the lack of bank stabilization. Other periods of missing record were from instrumentation malfunction.

Turbidity showed a consistent temporal variability between both study sites (fig. 8). During storm events with precipitation evenly distributed throughout the basin and not localized, measured turbidity values at both sites showed similar but lagged changes with time as the runoff moved downstream. The travel time of a runoff peak was approximately 18 hours between sites. In some instances, a larger streamflow and greater turbidity values would be noted at the downstream site compared to the upstream site. It is possible that more localized storms in the downstream reaches of Big River caused an increase in streamflow. No streamgage exists on Mineral Fork to determine its contribution of streamflow and suspended sediment to the Big River. The low-head mill dam just upstream from the downstream site was observed to restrict streamflow during low-flow conditions and resulted in turbidity values that differed from those at the upstream site.



**Figure 7.** Daily mean water temperature measured at two study sites on the Big River, Missouri, October 2011–September 2013.



Figure 8. Daily mean turbidity measured at two study sites on the Big River, Missouri, October 2011–September 2013.

## **Suspended-Sediment Quantity**

Discrete suspended-sediment concentrations were collected at each site at least monthly and during stormflow events (fig. 9). Samples were collected for the computation of daily SSC and SSL and were used to calibrate the regression model with the continuous turbidity data. During the 2012 water year, 11 individual base-flow and 4 sets of event SSC samples were collected at both sites (table 6); however, the November 2011 event collected at the downstream site did not have enough sediment mass for trace-element analyses and was not used for any event-based computations. During the 2013 water year, 7 individual base-flow and 3 sets of event SSC samples were collected at both sites (table 6). Base-flow SSC values ranged from 1 to 74 milligrams per liter (mg/L) at the upstream site during the study period, and event SSC values ranged from 74 to 1,091 mg/L (table 6; fig. 9). At the downstream site, base-flow SSC ranged from 4 to 127 mg/L and event SSC ranged from 27 to 871 mg/L (table 6; fig. 9). A previous study within the Ozark Plateaus (Davis and Bell, 1998) determined that median base-flow SSC ranged from 3 to 28 mg/L in streams of similar basin size and physiography, with increased SSC during increased streamflow. The median base-flow SSC for the upstream and downstream site during the study period was 10 mg/L and 13 mg/L, respectively (table 6).



**Figure 9.** Continuous streamflow and discrete suspended-sediment concentration samples collected at two study sites on the Big River, Missouri, October 2011–September 2013.

**Table 6.**Concentrations and size distributions of suspended-sediment samples collected at two study sites onthe Big River, Missouri, October 2011–September 2013.

[g, gram; mg/L, milligram per liter; %, percent; <, less than; mm, millimeter; --, not measured]

Sample date and time	Hydrologic event	Total sample dry mass (q)	Suspended-sediment concentration (mg/L)	Suspended sediment (% <0.063 mm)
	Big River below	Bonne Terre, Missouri (	07017610; upstream site)	
10/12/2011 16:40	base flow	0.005	4	
11/10/2011 12:15	base flow	0.003	2	
12/05/2011 18:00	base flow	0.052	20	
12/15/2011 11:15	rise	0.530	220	93.8
12/15/2011 11:40	rise	0.707	228	87.8
12/15/2011 12:20	peak	0.596	178	94.9
12/15/2011 13:50	peak	0.489	151	98.0
12/15/2011 14:00	fall	0.478	183	97.8
12/15/2011 15:00	fall	0.454	153	96.2
01/10/2012 13:50	base flow	0.002	1	
02/04/2012 16:45	base flow	0.328	74	
03/15/2012 11:15	base flow	0.010	6	
03/16/2012 10:50	rise	1.408	300	89.0
03/16/2012 15:15	rise	0.660	178	90.1
03/17/2012 00:01	peak	4.382	572	75.8
03/17/2012 16:40	fall	1.092	129	85.7
04/04/2012 16:15	base flow	0.012	10	
04/16/2012 06:30	rise	0.939	153	95.6
04/16/2012 10:40	peak	0.764	201	95.5
04/17/2012 13:50	fall	0.641	312	98.3
05/21/2012 16:30	base flow	0.012	10	
06/26/2012 12:45	base flow	0.008	10	
07/31/2012 10:35	base flow	0.004	7	
08/21/2012 15:30	base flow	0.005	7	
09/08/2012 14:15	rise	2.352	541	77.5
09/08/2012 16:40	peak	2.075	450	75.1
09/10/2012 13:00	fall	0.175	74	97.1
10/16/2012 11:30	base flow	0.052	26	
11/19/2012 12:00	base flow	0.005	4	
12/17/2012 12:15	base flow	0.002	2	
01/30/2013 11:20	rise	3.802	572	92.0
03/18/2013 11:30	peak	3.080	268	96.6
03/18/2013 15:50	peak	3.342	379	96.6
04/18/2013 13:32	rise	4.703	1,091	89.0
04/19/2013 09:14	peak	1.300	289	94.4
04/19/2013 11:24	fall	0.801	228	92.6
05/06/2013 14:30	base flow	0.238	57	
06/26/2013 15:30	base flow	0.024	12	
07/16/2013 10:40	base flow	0.021	23	
08/28/2013 11:00	base flow	0.022	13	
		minimum base flow	1	
		maximum base flow	74	
		median base flow	10	
		minimum stormflow	74	75.1
		maximum stormflow	1091	98.3
		median stormflow	228	94 1

**Table 6.**Concentrations and size distributions of suspended-sediment samples collected at two study sites onthe Big River, Missouri, October 2011–September 2013.—Continued

[g, gram; mg/L, milligram per liter; %, percent; <, less than; mm, millimeter; --, not measured]

Sample date and time	Hydrologic event	Total sample dry mass (g)	Suspended-sediment concentration (mg/L)	Suspended sediment (% <0.063 mm)
	Big River at Byr	nesville, Missouri (0701	8500; downstream site)	
10/13/2011 15:00	base flow	0.067	21	
11/10/2011 15:00	base flow	0.238	127	
11/22/2011 13:00	rise	0.106	34	
11/22/2011 13:30	rise	0.084	29	
11/22/2011 13:50	peak	0.078	27	
12/05/2011 12:40	base flow	0.047	17	
02/28/2012 10:15	base flow	0.018	6	
03/15/2012 15:10	base flow	0.035	17	
03/17/2012 12:40	rise	1.330	392	92.6
03/17/2012 20:45	peak	2.722	408	95.0
03/18/2012 13:20	fall	1.732	260	94.1
04/04/2012 12:50	base flow	0.029	14	
04/17/2012 10:25	peak	0.889	306	98.0
05/21/2012 13:37	base flow	0.033	19	
06/26/2012 15:00	base flow	0.010	9	
06/26/2012 15:05	base flow	0.009	10	
07/31/2012 13:45	base flow	0.005	6	
08/21/2012 10:10	base flow	0.008	9	
09/10/2012 10:15	fall	0.326	103	94.3
10/16/2012 08:50	base flow	0.023	12	
11/30/2012 10:00	base flow	0.005	4	
12/17/2012 13:45	base flow	0.004	4	
01/30/2013 16:45	rise	4.659	700	93.2
01/31/2013 08:30	rise	3.308	438	93.4
03/19/2013 18:00	peak	2.958	432	58.6
04/18/2013 16:03	rise	4.194	871	90.3
04/20/2013 16:15	peak	1.445	174	98.1
05/28/2013 09:30	base flow	0.126	44	
06/26/2013 11:30	base flow	0.029	11	
07/16/2013 12:00	base flow	0.039	25	
08/28/2013 13:40	base flow	0.044	23	
		minimum base flow	4	
		maximum base flow	127	
		median base flow	13	
		minimum stormflow	27	58.6
		maximum stormflow	871	98.1
		median stormflow	306	93.7

### Daily Suspended-Sediment Concentrations and Loads

The upstream and downstream sites had similar SSC and SSL extremes during the study, but these extremes did not always occur during the same stormflow events (figs. 10, 11). During the 2012 water year, the maximum daily mean SSC of 617 mg/L and maximum daily mean SSL of 2,920 tons at the upstream site occurred on September 8, 2012, whereas the maximum daily mean SSC of 522 mg/L and SSL of 6,120 tons at the downstream site occurred on March 18, 2012 (table 7). The maximum daily streamflow as shown in table 4 for the

upstream site did not occur on the same event as the maximum daily mean SSC during the 2012 water year, but did occur on the same event during the 2013 water year (fig. 10). One possible explanation is that even though the streamflow was less than the water year maximum during the event on September 8, 2012, the amount of available suspended sediments in the system and the time between large events were greater, resulting in higher turbidity measurements and SSC results for that event. During the 2013 water year, the maximum daily mean SSC and streamflows both occurred on the March 18, 2013, event at the upstream site (tables 4, 7). Maximum daily mean SSC and streamflows occurred on the same events during both study years for the downstream site (table 4, 7).



**Figure 10.** Daily mean suspended-sediment concentrations computed at two study sites on the Big River, Missouri, October 2011–September 2013.

Annual SSLs were computed to estimate the total amount of suspended sediments that passed the sites for each water year. The annual SSL increased greatly during the study period because the first water year (2012) was classified as a drought year whereas more precipitation was recorded during the 2013 water year. The upstream site had an annual SSL of 10,035 tons during the 2012 water year, which increased to 191,294 tons for the 2013 water year, and the downstream site had an annual SSL of 21,612 tons in 2012, which increased to 333,717 tons for the 2013 water year (table 7).

A previous study along the Black River in southeast Missouri (Barr, 2009) also computed annual SSL for an Ozark stream to assess damage from an upstream reservoir embankment breach. The study site, Black River below Annapolis, Mo. (USGS site number 07061600), has a drainage area of 493 mi<sup>2</sup>, which is similar to the drainage area of the Big River upstream site (409 mi<sup>2</sup>). The total annual SSL at the Black River site was 29,300 tons during the 2006 water year when sediment sources were readily available, but decreased to 17,400 tons during the 2007 water year because the readily available suspended sediments had been transported through the basin. The short-term effects of the damaged reservoir still did not cause large sediment volumes in comparison to the historical mining effects within the Old Lead Belt.



Figure 11. Daily mean suspended-sediment loads computed at two study sites on the Big River, Missouri, October 2011–September 2013.

 Table 7.
 Daily suspended-sediment concentration and load statistics at two study sites on the Big River, Missouri, October 2011–September 2013.

[mg/L, milligram per liter; E, estimated]

Water year <sup>1</sup>	Maximum daily mean suspended-sediment concentration (mg/L) and date		Minimum daily mean suspended-sediment concentration (mg/L) and date(s)		Maximu suspen load (te	um daily mean ded-sediment ons) and date	Minimum suspende load (tor	n daily mean ed-sediment us) and date	Annual suspended- sediment load (tons)	Number of estimated days
Big River below Bonne Terre, Missouri (07017610; upstream site)										
2012	617	September 8, 2012	2	many days	2,920	September 8, 2012	E 0.134	August 11, 2012	10,035	59
2013	E 1,010	March 18, 2013	E 3	August 11, 2013	E 50,500	March 18, 2013	0.526	December 9, 2012	191,294	73
			Big	River at Byrnesville	, Missouri (	07018500; downst	ream site)			
2012	522	March 18, 2012	2	July 27–29, 2012	6,120	March 18, 2012	0.281	July 28, 2012	21,612	0
2013	E 927	April 20, 2013	3	December 22, 30, 31, 2012, January 1–9, 2013	E 66,000	April 20, 2013	1.77	January 8, 2013	333,717	62

<sup>1</sup>Water year is defined as the 12-month period beginning October 1 and ending September 30 of the calendar year in which it ends (water year 2012 is the period October 1, 2011 through September 30, 2012).

## **Event-Based Suspended-Sediment Concentrations, Load, and Yields**

For all stormflow events sampled during the study period, an event-based average SSC and SSL were computed to help determine the mass of suspended sediments transported during each sampled event. Averaged event SSCs ranged from approximately 100 mg/L to 1,400 mg/L at both study sites (table 8). Event SSLs ranged from about 180 to 32,000 tons at the upstream site and from about 390 to 53,000 tons at the downstream site (table 8). Most events lasted more than 24 hours, and the same hydrologic event was sampled at both sites, except the December 15, 2011, event, when only the upstream site was sampled (table 8). The December 2011 event was more localized in the upper portion of the watershed resulting in only a minor event by the time the event reached the downstream site. Event-specific SSLs were greater at the downstream site except for the September 2012 event, and event yields were greater at the upstream site than the downstream site during all events except April 2012 (table 8). Event loads and yields were greater during water year 2013 events, with the April 2013 event having the greatest loads and yields at both sites (table 8). It is possible that the large differences in event yields between sites are because of limited SSC collections during events at the downstream site, and because more sediments are available in the upper part of the basin closer to the historical mining activity. It should be noted that events differed in intensity and duration between the study sites, such as April 2012 (40 hours at the upstream site and 63 hours at the downstream site), which could cause some bias in comparisons. Events at the downstream site were very slow

moving and occurred over multiple days, but turbidity values did not show much variation at times, which made predictions of an event with sufficient, available suspended sediments difficult to determine. All event-based concentrations, loads, and yields are most likely biased low because of limited number of samples collected during the event but can be useful in approximating the minimum volume of suspended sediments transported downstream during stormflow events.

Even though a limited number of events could be sampled, using the continuous turbidity data to compute the daily SSL in conjunction with event sampling provided adequate data to determine the majority of the SSL in Big River occurs during stormflow events. Not all stormflow events that occurred during the study period could be sampled, yet the events that were sampled make up a considerable portion of the annual SSL. Because the SSCs collected during base-flow conditions during the study period are generally very low (typically less than 50 mg/L at both sites), a general base-flow SSL can be computed for each site to compare to event-based SSLs. The median of all daily median streamflow values for the upstream site during the study period (132 ft<sup>3</sup>/s) was used to represent a base streamflow condition. Using the median streamflow and a SSC of 50 mg/L, an annual base-flow SSL for the study period can be derived as 18 tons, and the total SSL of the seven events sampled at the upstream site during the study period is about 57,700 tons (table 8). When compared to the sum of annual SSLs computed from the regression model for the study period (table 7), the base-flow SSL accounts for less than 0.01 percent and the sampled events account for about 29 percent of the total SSL at the upstream site. For the downstream site, the base streamflow computed

Table 8.Suspended-sediment concentrations, loads, and yields from sampled stormflow events at two study sites on the Big River,Missouri, October 2011–September 2013.

				Suspended-sediment					
Event date	Event duration (hr)	Event number	Sampled runoff volume (ft³)	Average event	Lo	Yield (lb/mi²)/hr			
				(mg/L)	(lb)	(ton)	_		
		Big River bel	ow Bonne Terre, M	issouri (07017610;	upstream site)				
Dec. 15, 2011	19	1	50,150,000	1,110	354,000	177	522		
Mar. 16–17, 2012	39.75	2	343,000,000	1,180	7,000,000	3,330	1,540		
Apr. 16, 2012	23.75	3	49,110,000	354	352,000	176	125		
Sept. 8-9, 2012	42.50	4	226,000,000	991	4,000,000	1,840	1,240		
Jan. 29-31, 2013	38.75	5	740,000,000	572	13,200,000	6,590	1,670		
Mar. 17–19, 2013	54	6	2,000,000,000	647	26,600,000	13,300	5,490		
Apr. 18–19, 2013	51	7	2,210,000,000	1,380	64,600,000	32,300	9,510		
		Big River at	Byrnesville, Misso	uri (07018500; dow	nstream site)				
Mar. 17–18, 2012	39.75	1	474,000,000	1,060	8,600,000	4,300	801		
Apr. 15–18, 2012	63	2	510,000,000	306	4,900,000	2,430	161		
Sept. 9-10, 2012	39.50	3	244,000,000	103	781,000	391	47.8		
Jan. 30–31, 2013	35.50	4	759,000,000	919	23,200,000	11,600	1,520		
Mar. 17–20, 2013	76.75	5	4,600,000,000	432	62,400,000	31,200	1,840		
Apr. 18–20, 2013	53.50	6	3,300,000,000	958	110,000,000	53,100	2,920		

[hr, hour; ft3, cubic foot; mg/L, milligram per liter; lb, pound; mi2, square mile; (lb/mi2)/hr, pound per square mile per hour]

for the study period was 339 ft<sup>3</sup>/s. Using the same base-flow SSC of 50 mg/L, the annual base-flow SSLs were 46 tons during the study period, accounting for about 0.01 percent of the total SSL computed from the regression model (table 7). The six events sampled at the downstream site had a combined SSL of about 103,000 tons (table 8), or about 29 percent of the total SSL for the study period.

# **Suspended-Sediment Quality**

Suspended sediments collected during event sampling were more abundant in the fines fraction (tables 6 and 9). The supply of materials finer than bed material that are in suspension (also known as the "wash load") usually have a greater effect on the SSC than streamflow conditions, because the rate of supply varies during and between events as well as from seasonal precipitation and vegetation (Charlton, 2008). Increases in streamflow produce increased SSC as erosion increases, releasing finer particles from storage and increasing the stream's capacity for sediment transport. The event samples collected at the upstream site were 75 to 98 percent fines and the event samples collected at the downstream site were from 90 to 98 percent fines in all samples except one (table 6). Only one sample during the entire study, collected at

the downstream site on the peak of the March 19, 2013, event, was less than 75 percent (59 percent) fines (table 6).

## Selected Trace-Element Concentrations in Suspended Sediments

The laboratory results of event samples with adequate sample mass for analysis are listed in table 9 and include four selected trace-element concentrations-barium, cadmium, lead, and zinc. The four trace elements were selected for inclusion in this report because they are contained in ore minerals mined in the Big River Basin and are readily available for transport from both natural-source erosion and from mine waste. In addition, cadmium, lead, and zinc are considered toxic to aquatic life at certain concentrations in bed sediments and in dissolved form (MacDonald and others, 2000). The primary minerals containing barium, cadmium, lead, and zinc are relatively insoluble and predominately are found in the solid phase (Smith and Schumacher, 1991; 1993). No samples for dissolved trace-element concentrations were collected during the study period to include in the total concentration computation of trace elements at the study sites. Smith and Schumacher (1991; 1993) collected dissolved trace element concentrations at a site along the Big River near Desloge

 Table 9.
 Selected trace-element concentrations for two particle size distributions of suspended sediments collected during stormflow events at two study sites on the Big River, Missouri, October 2011–September 2013.

[sand, sediment greater than 0.063 millimeters; fines, sediment less than 0.063 millimeters; mg/kg, milligram per kilogram; --, not available]

			Trace element concentrations in suspended sediments								
Event	Sample	Sample	Bai	rium	Cadı	Cadmium Lead			Zi	nc	
number	date	time	Sand (mg/kg)	Fines (mg/kg)	Sand (mg/kg)	Fines (mg/kg)	Sand (mg/kg)	Fines (mg/kg)	Sand (mg/kg)	Fines (mg/kg)	
			Big River	below Bonne	Terre, Missou	uri (07017610;	upstream site	)			
1	12/15/2011	11:15		640		10		1,000		1,000	
	12/15/2011	11:40		670		9		900		910	
	12/15/2011	12:20		700		9		880		900	
	12/15/2011	13:50		700		8		750		860	
	12/15/2011	14:00		750		7		680		780	
	12/15/2011	15:00		730		7		680		760	
2	03/16/2012	10:50		580		10		890		780	
	03/16/2012	15:15		580		11		1,100		980	
	03/17/2012	00:01	240	600	8	16	750	1,700	470	1,000	
	03/17/2012	16:40		550		15		1,700		1,100	
3	04/16/2012	06:30		520		12		1,200		1,100	
	04/16/2012	10:40		520		9		750		750	
4	09/08/2012	14:15	280	540	30	35	1,400	2,400	1,200	1,800	
	09/08/2012	16:40	270	610	23	33	1,000	2,300	910	1,600	
5	01/30/2013	11:20	340	660	12	10	1,000	980	620	670	
6	03/18/2013	11:30		560		11		1.300		680	
	03/18/2013	15:50		590		12		1.200		620	
7	04/18/2013	13:32	410	580	5	4	810	690	680	720	
	04/19/2013	09.14		560		14		1 500		790	
	Minimum		240	520	5	4	750	680	470	620	
	Median		280	590	12	10	1 000	1 000	680	860	
	Mean		308	613	16	13	002	1 1 8 9	776	037	
	Maximum		410	750	30	35	1 400	2 400	1 200	1 800	
	Maximum		Rig Rive	r at Ryrnosvil	Jo Missouri (N	7018500: dow	nstroam sito)	2,400	1,200	1,800	
1	03/17/2012	12.40		1 200		4		540		290	
1	03/17/2012	20.45		1,200		т 1		960		480	
	03/18/2012	13.20		1,200		4		1 100		570	
2	04/17/2012	10.25		1,100		3		700		440	
2	09/10/2012	10.25		1,300		7		1 800		760	
3	01/30/2012	16:45	740	1,300		1		1,000	470	/00	
4	01/2012	08.20	/40	1,300	/	4	940	1,000	470	500	
5	01/31/2013	18.00		050		0		1,100		500	
5	03/19/2013	16.00	43	930		0	55	260	51	250	
0	04/18/2013	10:03		/40		2		300 1.500		250	
	04/20/2013	10:15		920		8		1,500		080	
	Madia		45	/40		2	55	360	51	250	
	Median			1,200		5		1,050		490	
	Mean		393	1,141	7	5	497/	1,075	251	501	
	Maximum	-	/40	1,500		8	940	1,800	470	/60	
Consensus-based sediment quality guidelines (MacD						nes (MacDona	aid and others	5, 2000)			
~		1.1 . 00			Cadmiun	n (mg/kg)	Lead (	mg/kg)	Zinc (	mg/kg)	
Consensu	Consensus-based threshold effect concentration (TEC)		TEC)	0.9	19	35.8		1	21		
Consensu	is-based probab	le effect con	centration (l	PEC)	4.9	0	128		4	59 40	
Foxic effe	ect threshold (T	ET)			3		1/0		2.	+V	

(fig. 1) during base flow and stormflow events, and total recoverable trace element concentrations only were collected during base flow conditions. The available dissolved trace element concentrations show the dissolved lead and zinc concentrations were very low, indicating a minimal portion of the total trace-element concentration would be from the dissolved phase. The full suites of trace element results for all samples are available on NWISWeb (http://nwis.waterdata.usgs.gov/mo/nwis/qwdata).

Events 2, 4, 5, and 7 collected at the upstream site and events 4 and 5 collected at the downstream site had enough mass in both the sand and fines fractions for complete analyses of the total suspended sediments collected (table 9; fig. 12). Barium concentrations in the sand fraction were less than the concentrations in the fines fraction at both sites. Cadmium concentrations in sands were less than the fines fraction except for event number 5 at the upstream site (12 milligrams per kilogram [mg/kg] in sands, 10 mg/kg in fines) and event 4 at the downstream site (7 mg/kg in sands, 4 mg/kg in fines), although the concentrations were similar (table 9). Events 5 and 7 at the upstream site had similar but slightly higher concentrations of lead in the sand fraction than the fines fraction during event 5 and event 7 (table 9), and only event 4 at the downstream site had slightly higher but similar zinc concentrations in the sand fraction than the fine fraction (table 9). The greatest differences between sand and fines fraction concentrations were noted in lead and zinc concentrations for events 2 and 4 at the upstream site (fig. 12). The peak sample collected during event 2 on March 17, 2012, had lead concentrations of 750 mg/kg in the sand fraction and 1,700 mg/kg in the fines fraction, and zinc concentrations of 470 mg/kg in sand and 1,000 mg/kg in the fines (table 9, fig. 12). Event number 4 at the upstream site, collected September 8, 2012, had lead concentrations in the sand on the rising limb sample of 1,400 mg/kg and 2,400 mg/kg in the fines. The sand in the peak sample had a lead concentration of 1,000 mg/kg and the fines had a concentration of 2,300 mg/kg (table 9; fig. 12). The highest concentrations of cadmium (30 mg/kg in sand, 35 mg/kg in fines) and zinc (1,200 mg/kg in sand, 1,800 mg/kg in fines) occurred during event number 4 at the upstream site.

During a previous study of surface water and sediment quality in the Old Lead Belt, trace-element concentrations in suspended sediments also were measured during events within the Big River Basin (Smith and Schumacher, 1991; 1993), but do not indicate any changes in selected concentrations between study periods. Three event samples were collected between September 1988 and February 1989 at the Big River below Desloge, Mo. (USGS site number 07017620; site 6 in Smith and Schumacher, 1993), located upstream from the study area for this report and downstream from the Desloge mine waste pile (fig. 1). Barium and cadmium concentrations at Desloge were similar to the upstream site concentrations and the lead and zinc concentrations at Desloge were higher than the upstream site concentrations. Barium concentrations in suspended sediments ranged from 390 to 630 mg/kg at Desloge and 240 to 750 mg/kg at the upstream site, and

cadmium concentrations ranged from 21 to 30 mg/kg at Desloge and 4 to 35 mg/kg at the upstream site (table 9). Lead concentrations in the three event samples at Desloge during the previous study ranged from 1,100 to 3,200 mg/kg and at the upstream site the lead concentrations ranged from 680 to 2,400 mg/kg. Zinc concentrations at Desloge ranged from 1,100 to 2,200 mg/kg, which were higher than the upstream site concentrations (470 to 1,800 mg/kg). The difference in sampling location, event intensity, changes in geomorphology of the stream, or remediation efforts of mine waste piles could be reasons lead and zinc concentrations were higher at Desloge than the upstream site. Not enough data are available to determine if any long-term decreases have occurred.

Sediment quality guidelines (SQG) for freshwater (Mac-Donald and others, 2000) describe two qualities of environmental effects from trace-element concentrations in suspended sediments-the threshold effect concentration (TEC) and the probable effect concentration (PEC). A TEC is defined as a concentration below which adverse effects are not expected to occur below, and a PEC is a concentration in which adverse effects are expected to occur at or above more often. Within these two sediment qualities are many levels and thresholds that help regulatory agencies assess the toxicity of sediments within a remediation study. The highest threshold in the PEC group is the toxic effect threshold (TET), which is the concentration above which sediment is considered to be heavily polluted causing adverse effects on sediment-dwelling organisms (MacDonald and others, 2000). Both TEC and PEC are consensus-based levels of concentration to reflect the intent of each SQG type. Although these threshold and probable effects are based on streambed sediments, comparisons were made with the stormflow event sediment results because these suspended sediments were most likely at rest on the streambed during base-flow conditions and after transport will be at rest again on the streambed.

Concentrations of cadmium, lead, and zinc in suspended sediment samples collected during stormflow events at both sites exceeded the consensus-based TEC and consensus-based PEC (fig. 12). All cadmium concentrations in the fine and sand fractions of suspended sediments at both sites exceeded the consensus-based TEC (0.99 mg/kg) and PEC (4.98 mg/kg). All lead and zinc concentrations in the fine fraction of all suspended sediment from both sites greatly exceeded the consensus-based TEC (35.8 mg/kg for lead; 121 mg/kg for zinc) and the PEC (128 mg/kg for lead; 459 mg/kg for zinc). Lead concentrations in the fine fraction of all samples at both sites also exceeded TET of 170 mg/kg. Zinc concentrations in the fine fraction for four of the five samples from the upstream site also exceeded the TET of 540 mg/kg (fig. 12). Lead and zinc concentrations in the sand fraction exceeded their respective consensus-based PECs except for the sand fraction of event number 5 collected at the downstream site.

Concentrations of cadmium and zinc were notably higher in suspended sediment samples from the upstream site compared to the downstream site, especially in the fine fraction. The smaller cadmium and zinc concentrations at

the downstream site could be a result of a decrease in source material enriched in these trace elements in the downstream areas of the watershed compared to the upstream area within the Old Lead Belt. Concentrations of lead, while variable, tended to be similar in both fractions at the two sites (fig. 12). The lead concentrations greatly exceeded the PEC as well as the TET, in some samples by a factor of 10, which indicates that lead-rich suspended sediments, especially in the fine fraction, are readily available for transport within the Big River Basin. These lead-enriched, finer sediments could remain in the system from historical mining, and as the capping of mine waste piles upstream from Bonne Terre continues to reduce additional sediment loadings, these fine sediments may be continually released as the river scours the streambed and erodes the stream banks causing lead-rich suspended sediment to remain in a state of equilibrium.



- - Consensus-based toxic effect threshold (TET; MacDonald and others, 2000)
- --- Consensus-based probable effect concentration level (PEC; MacDonald and others, 2000)
- --- Consensus-based threshold effect concentration level (TEC; MacDonald and others, 2000)
- Upstream site Big River below Bonne Terre, Missouri (07017610)
- Downstream site Big River at Byrnesville, Missouri (07018500)
  - Event number Numeric representation of stormflow events collected at each site during study period (table 9)

**Figure 12.** Trace-element concentrations in two suspended-sediment size fractions collected during stormflow events at two study sites on the Big River, Missouri, October 2011–September 2013.

Variation within the event sample concentrations was typically low, but some large variations were noted for cadmium, lead, and zinc during two events. Event 7 at the upstream site, collected April 18 and 19, 2013, showed high variation of cadmium and lead concentrations in the fines fraction of the samples (table 9). The two samples collected during this event were collected near two different streamflow peaks; the first sample occurred from localized runoff of a smaller tributary upstream from the site (categorized as a rise sample in table 6) and the second sample occurred from the main channel peak, which traveled from farther upstream (considered the actual peak for the event in table 6). The increase in cadmium and lead during the second sample could be because of more sources of these trace elements from upstream sources. During this same event, high variation among concentrations at the downstream site also were noted. The event sampling at the downstream site (event 6) occurred on the rise and near the peak of the event, during April 18 and 20, 2013. This particular stormflow event caused flooding conditions at the routine sampling site as the river crested, which made the normal sampling location inaccessible. The peak sample collection was performed approximately one-half mile downstream. This alternate location experienced overbank backflow conditions along the row crop and sod fields, which may account for the large increases in concentrations of selected trace elements (fig. 12).

Barium concentrations were nearly twice as high in event samples collected at the downstream site as compared to samples from the upstream site (fig. 12). It is probable the source of barium in the Big River comes from the Mineral Fork and Mill Creek, which flow through the historic, open-pit barite (barium sulfate, also known as tiff) mining district in Washington County. Mineral Fork is the largest tributary to the Big River between the two study sites.

In the case where both size fractions could be analyzed for trace-element concentrations, a total trace-element concentration was computed for the SSC sample. Concentrations of total trace elements (the computed total of concentrations from both the sand and fine fractions) in suspended sediments varied by site and event (table 10). Concentrations are likely affected by stream velocity, localized runoff, seasonality, and event duration and intensity. The maximum and minimum concentrations at both sites for total barium, cadmium, lead, and zinc occurred during different events and in some instances, the maximum concentration for the upstream site was the same event for which a minimum concentration was detected at the downstream site (table 10). The maximum barium concentration at the upstream site was 0.613 mg/L during event 7, whereas the barium concentration at the downstream site during the same event (event number 6 for the downstream site) was the second-smallest concentration detected at 0.157 mg/L. The maximum lead concentration of 1.18 mg/L (the largest concentration detected during the study for both sites) occurred during event 4 (September 2012) at the upstream site; however, the minimum lead concentration detected at the downstream site during this

same event on September 10, 2012 (downstream site event 3) was 0.174 mg/L. The difference in concentrations between the two sites during the same stormflow event could be the effect of limited sample collection on the stormflow hydrographs, as well as more localized runoff in the headwaters of Big River. It is also possible that increased streamflow from Mineral Fork during the event diluted concentrations as the flows moved downstream. The maximum zinc concentration at the upstream site was the largest zinc concentration detected during the study for both sites at 0.901 mg/L, which occurred during the study period was 0.074 mg/L and was detected during event 3 at the downstream site. The maximum concentrations of barium, cadmium, lead, and zinc at the downstream site all occurred during event number 4 (January 2013).

The mean total trace-element concentrations in suspended sediments from stormflow events were compared between both sites during the study period. Mean concentrations of cadmium and lead were similar for both sites with mean cadmium concentrations of 0.004 mg/L at the upstream site and 0.002 mg/L at the downstream site, and mean lead concentrations of 0.379 mg/L at the upstream site and 0.335 mg/L at the downstream site (table 10). Mean barium concentrations were higher at the downstream site (0.411 mg/L) than at the upstream site (0.184 mg/L). As noted previously, it is probable that a large source of barium enters the Big River from the Mineral Fork and Mill Creek, which drain a historical, openpit barite mining region. The mean zinc concentrations in the suspended sediments were higher upstream in the Big River than downstream, with a mean concentration of 0.291 mg/L at the upstream site, and mean concentration of 0.162 mg/L at the downstream site (table 10).

Seasonal comparisons of event-based lead and zinc concentrations in suspended sediments also were used for analyses of sediment quality in the Big River, though the study period was not long enough to provide extensive data for comparisons. The seasonal comparison boxplots of SSC show that more event samples were collected in winter at the upstream site than at the downstream site (fig. 13). The large number of samples in winter at the upstream site is because the first event collected at the upstream site was a pilot sampling event to ensure proper and consistent methods could be used during stormflow events and to determine the volume of sample needed to have adequate mass for trace-element analyses. Spring was the most-sampled season at both sites during the study period, because stormflow events tend to occur in the wetter spring months. Median lead and zinc concentrations collected in spring were similar at both sites, whereas median concentrations of lead and zinc were greatest in fall at the upstream site and greatest in winter at the downstream site (fig. 13). It is possible that the median concentrations in the fall were greater at the upstream site because the fall event from September 2012 was the first seasonal event in several months and the large amount of precipitation in the area of the site caused an increase in runoff. The winter event at the downstream site occurred in January 2013, after the removal

**Table 10.** Streamflow, suspended-sediment concentrations and particle-size distributions, and selected total trace-elementconcentrations in suspended sediments collected during stormflow events at two study sites on the Big River, Missouri,October 2011–September 2013.

[ft<sup>3</sup>/s, cubic foot per second; mg/L, milligram per liter; %, percent; >, greater than; mm, millimeter; <, less than]

_		Sample	Stream-	Su	spended sedi	ment	Total trace	Total trace element concentration in suspended sediments (mg/L)				
Event	Sample date	Sample	flow	Concen-	Sand	Fines						
nunnei		une	(ft³/s)	tration (mg/L)	(% >0.063 mm)	(% <0.063 mm)	Barium	Cadmium	Lead	Zinc		
			Big River	below Bonn	e Terre, Misso	uri (07017610;	upstream site	)				
1	12/15/2011	11:15	1,000	220	6.2	93.8	10.132	10.002	<sup>1</sup> 0.206	<sup>1</sup> 0.206		
	12/15/2011	11:40	965	228	12.2	87.8	10.134	10.002	<sup>1</sup> 0.180	<sup>1</sup> 0.182		
	12/15/2011	12:20	928	178	5.1	94.9	<sup>1</sup> 0.119	10.002	<sup>1</sup> 0.149	10.152		
	12/15/2011	13:50	818	151	2.0	98.0	10.104	10.001	<sup>1</sup> 0.111	<sup>1</sup> 0.127		
	12/15/2011	14:00	798	183	2.2	97.8	<sup>1</sup> 0.134	10.001	10.122	<sup>1</sup> 0.140		
	12/15/2011	15:00	750	153	3.8	96.2	<sup>1</sup> 0.107	10.001	<sup>1</sup> 0.100	10.112		
2	03/16/2012	10:50	1,350	300	11.0	89.0	<sup>1</sup> 0.155	10.003	<sup>1</sup> 0.237	<sup>1</sup> 0.208		
	03/16/2012	15:15	1,370	178	9.9	90.1	<sup>1</sup> 0.093	10.002	<sup>1</sup> 0.176	<sup>1</sup> 0.157		
	03/17/2012	00:01	4,730	572	24.2	75.8	<sup>2</sup> 0.293	<sup>2</sup> 0.008	<sup>2</sup> 0.841	<sup>2</sup> 0.498		
	03/17/2012	16:40	1,690	129	14.3	85.7	<sup>1</sup> 0.061	10.002	<sup>1</sup> 0.188	<sup>1</sup> 0.122		
3	04/16/2012	06:30	547	153	4.4	95.6	<sup>1</sup> 0.076	<sup>1</sup> 0.002	<sup>1</sup> 0.176	10.161		
	04/16/2012	10:40	813	201	4.5	95.5	10.100	<sup>1</sup> 0.002	10.144	10.144		
4	09/8/2012	14:15	2,890	541	22.5	77.5	<sup>2</sup> 0.261	<sup>2</sup> 0.018	<sup>2</sup> 1.18	<sup>2</sup> 0.901		
	09/8/2012	16:40	3,390	450	24.9	75.1	<sup>2</sup> 0.236	<sup>2</sup> 0.014	<sup>2</sup> 0.888	<sup>2</sup> 0.642		
5	01/30/2013	11:20	6,470	572	8.0	92.0	<sup>2</sup> 0.363	<sup>2</sup> 0.006	<sup>2</sup> 0.561	<sup>2</sup> 0.381		
6	03/18/2013	11:30	20,100	268	3.4	96.6	10.145	<sup>1</sup> 0.003	<sup>1</sup> 0.337	<sup>1</sup> 0.176		
	03/18/2013	15:50	18,600	379	3.4	96.6	10.216	10.004	<sup>1</sup> 0.440	<sup>1</sup> 0.227		
7	04/18/2013	13:32	11,600	1,091	11.0	89.0	<sup>2</sup> 0.613	<sup>2</sup> 0.004	<sup>2</sup> 0.767	<sup>2</sup> 0.781		
	04/19/2013	09:14	21,900	289	5.6	94.4	10.153	10.004	<sup>1</sup> 0.409	10.216		
		Median	1,370	228	6.2	93.8	0.134	0.002	0.206	0.182		
		Mean	5,300	328	9.4	90.6	0.184	0.004	0.379	0.291		
			Big Rive	r at Byrnesvi	lle, Missouri (	07018500; dow	nstream site)					
1	03/17/2012	12:40	1,760	392	7.4	92.6	10.436	<sup>1</sup> 0.001	<sup>1</sup> 0.196	<sup>1</sup> 0.105		
	03/17/2012	20:45	3,380	408	5.0	95.0	<sup>1</sup> 0.465	<sup>1</sup> 0.002	<sup>1</sup> 0.372	<sup>1</sup> 0.186		
	03/18/2012	13:20	4,330	260	5.9	94.1	<sup>1</sup> 0.269	<sup>1</sup> 0.001	<sup>1</sup> 0.269	10.140		
2	04/17/2012	10:25	2,410	306	2.0	98.0	10.450	10.001	<sup>1</sup> 0.237	10.132		
3	09/10/2012	10:15	1,490	103	5.7	94.3	10.126	<sup>1</sup> 0.001	<sup>1</sup> 0.174	<sup>1</sup> 0.074		
4	01/30/2013	16:45	6,050	700	6.8	93.2	<sup>2</sup> 0.884	<sup>2</sup> 0.003	<sup>2</sup> 0.698	<sup>2</sup> 0.316		
	01/31/2013	08:30	10,800	438	6.6	93.4	<sup>1</sup> 0.490	<sup>1</sup> 0.002	<sup>1</sup> 0.449	10.204		
5	03/19/2013	18:00	27,300	432	41.4	58.6	<sup>2</sup> 0.248	<sup>2</sup> 0.002	<sup>2</sup> 0.414	<sup>2</sup> 0.155		
6	04/18/2013	16:03	7,930	871	9.7	90.3	10.582	<sup>1</sup> 0.002	10.283	<sup>1</sup> 0.197		
	04/20/2013	16:15	26,700	174	1.9	98.1	<sup>1</sup> 0.157	<sup>1</sup> 0.001	<sup>1</sup> 0.256	<sup>1</sup> 0.116		
		Median	5,190	400	6.3	93.7	0.443	0.002	0.276	0.147		
		Mean	9,215	408	9.3	90.7	0.411	0.002	0.335	0.162		

<sup>1</sup>Concentration computed from fines only.

<sup>2</sup>Concentrations computed from both sands and fines.



Figure 13. Seasonal comparison of stormflow-event suspended-sediment concentrations and mass-accumulation lead and zinc concentrations within suspended sediments for two study sites on the Big River, Missouri, October 2011–September 2013.

of vegetation from the banks near the streamgage location, which could have increased the available suspended sediments during runoff. No events were sampled during summer months within the study period.

## Event-Based Loads and Yields of Selected Trace-Element Concentrations in Suspended Sediments

Results of the four selected trace-element event-based average concentrations and the event-based load and yields are shown in table 11. Event-based loads computed at the upstream site were largest for all four constituents during April 2013 (event 7), with the lead load being the largest with 29.4 tons transported during the event. There was minimal decrease in the corresponding lead load at the downstream site, where the event-based load was 27.1 tons. The largest event-based lead load for the downstream site was 29.9 tons during event 5 in March 2013.

An event-based yield also was computed to make the study sites more comparable by normalizing the drainage areas and event durations. Event-based yields were larger at the upstream site (table 11). Two events showed similar lead and zinc yields for both sites—April 2012 and January 2013. The largest event-based lead yield at the upstream site was 8.17 pounds per square mile per hour during event 7. The downstream site had smaller yields, with the largest event-based lead yield being 1.76 pounds per square mile per hour during event 5.

**Table 11.**Selected trace element concentrations, loads, and yields in suspended sediments from sampled stormflow events at twostudy sites on the Big River, Missouri, October 2011–September 2013.

[hr, hour; mg/L, milligrams per liter; lb, pound; mi<sup>2</sup>, square mile; lb/mi<sup>2</sup>/hr, pounds per square mile per hour]

		Trace element in suspended sediments						
Event	Event date	Event duration		Average event	Loa	d	Vield	
number		(hr)	Constituent	concentration (mg/L)	(lb)	(ton)	(lb/mi²/hr)	
		Big River belo	w Bonne Terre, N	lissouri (07017610; ups	tream site)			
1	Dec. 15, 2011	19	Barium	0.677	164	0.082	0.322	
			Cadmium	0.009	2.88	0.001	0.004	
			Lead	0.869	284	0.142	0.412	
			Zinc	0.920	298	0.149	0.434	
2	Mar. 16–17, 2012	39.75	Barium	0.602	3,395	1.70	0.789	
			Cadmium	0.014	88.3	0.04	0.020	
			Lead	0.942	5,944	2.97	1.10	
			Zinc	0.985	5,825	2.91	1.32	
3	Apr. 16, 2012	23.75	Barium	0.176	175	0.088	0.062	
			Cadmium	0.003	3.31	0.002	0.001	
			Lead	0.319	295	0.147	0.111	
			Zinc	0.305	285	0.143	0.106	
4	Sept. 8–9, 2012	42.50	Barium	0.497	1,885	0.943	0.620	
			Cadmium	0.032	116	0.058	0.040	
			Lead	2.07	7,512	3.76	2.58	
			Zinc	1.54	5,536	2.77	1.93	
5	Jan. 29–31, 2013	38.75	Barium	0.363	8,355	4.18	1.06	
			Cadmium	0.006	134	0.067	0.017	
			Lead	0.561	12,930	6.46	1.64	
			Zinc	0.381	8,772	4.39	1.11	
6	Mar. 17–19, 2013	54	Barium	0.361	14,776	7.39	3.06	
			Cadmium	0.007	295	0.148	0.061	
			Lead	0.776	32,180	16.09	6.59	
			Zinc	0.403	16,737	8.37	3.42	
7	Apr. 18–19, 2013	51	Barium	0.765	35,655	17.83	5.27	
			Cadmium	0.008	437	0.218	0.058	
			Lead	1.18	58,846	29.42	8.17	
			Zinc	0.996	46,808	23.40	6.87	
			Barium		5,619	2.81	1.79	
			Cadmium		211	0.105	0.065	
		Water year <sup>1</sup> 2012	Lead		14,034	7.02	4.20	
	Annual total of		Zinc		11,945	5.97	3.79	
	sampled events		Barium		58,785	29.39	9.39	
		1	Cadmium		866	0.433	0.136	
		Water year <sup>1</sup> 2013	Lead		103,956	51.98	16.39	
			Zinc		72,317	36.16	11.40	

**Table 11.**Selected trace element concentrations, loads, and yields in suspended sediments from sampled stormflow events at twostudy sites on the Big River, Missouri, October 2011–September 2013.—Continued

[hr, hour; mg/L, milligrams per liter; lb, pound; mi<sup>2</sup>, square mile; lb/mi<sup>2</sup>/hr, pounds per square mile per hour]

	Event date	Event duration (hr)	Trace element in suspended sediments				
Event number			Constituent	Average event concentration (mg/L)	Load		Vield
					(Ib)	(ton)	(lb/mi²/hr)
Big River at Byrnesville, Missouri (07018500; downstream site)							
1	Mar. 17–18, 2012	39.75	Barium	1.17	9,461	4.73	0.879
			Cadmium	0.004	38	0.019	0.004
			Lead	0.838	7,649	3.82	0.690
			Zinc	0.431	3,905	1.95	0.354
2	Apr. 15–18, 2012	63	Barium	0.450	7,158	3.58	0.237
			Cadmium	0.001	14.3	0.007	0.000
			Lead	0.237	3,770	1.88	0.125
			Zinc	0.132	2,100	1.05	0.070
3	Sept. 9–10, 2012	39.50	Barium	0.126	958	0.479	0.059
			Cadmium	0.001	5.16	0.003	0.000
			Lead	0.174	1,327	0.663	0.081
			Zinc	0.074	560	0.280	0.034
4	Jan. 30–31, 2013	35.50	Barium	1.13	28,357	14.2	1.86
			Cadmium	0.004	101	0.050	0.007
			Lead	0.922	23,325	11.7	1.53
			Zinc	0.418	10,580	5.29	0.695
5	Mar. 17–20, 2013	76.75	Barium	0.248	35,864	17.9	1.06
			Cadmium	0.002	292	0.146	0.009
			Lead	0.414	59,814	29.9	1.76
			Zinc	0.155	22,352	11.2	0.659
6	Apr. 18-20, 2013	53.50	Barium	0.661	75,034	37.5	2.04
			Cadmium	0.002	296	0.148	0.008
			Lead	0.411	54,254	27.1	1.39
			Zinc	0.255	31,576	15.8	0.830
	Annual total of	Water year <sup>1</sup> 2012	Barium		17,577	8.79	1.18
			Cadmium		57	0.029	0.004
			Lead		12,745	6.37	0.90
			Zinc		6,565	3.28	0.46
sampled eve	sampled events	Water year <sup>1</sup> 2013	Barium		139,255	69.6	4.95
			Cadmium		689	0.344	0.023
			Lead		137,393	68.7	4.69
			Zinc		64,509	32.3	2.18

<sup>1</sup>Water year is defined as the 12-month period beginning October 1 and ending September 30. The water year is designated by the calendar year in which it ends and contains 9 of the 12 months.

Loads computed during the study period for sampled events were higher at the downstream site and yields were higher at the upstream site. As previously noted, computed annual runoff was greater at the upstream site than the downstream site. In addition, stormflow events at the downstream site had much longer durations and lower velocities than events at the upstream site. It is possible that the lowhead dam just upstream from the sampling location at the downstream site slowed the stream velocity enough to cause sediments to fall out of suspension and be deposited on the streambed before reaching the sampling location. Other possible effects could be localized precipitation and fewer areas affected by mining activities in the downstream part of the Big River Basin. The additional volume of streamflow from Mineral Fork could dilute some trace-element concentrations downstream, though it is difficult to determine the amount of influence to the Big River because no streamgages are in operation on this tributary. The decreases in loads from the upstream to the downstream site also could be an artifact of the limited number of event samples that could be collected at the downstream site.

Total trace-element loads and yields in suspended sediments were computed from the sampled events for each year in the study. Although no trace-element concentrations were collected during base-flow conditions, SSCs during base-flow typically were less than 50 mg/L and the majority of suspended sediments are transported through the Big River during stormflow events. Given the affinity of trace elements to be transported with sediments (Horowitz and Elrick, 1987), it is likely that the majority of the selected trace elements in suspended sediments are transported during runoff events as well. Using these assumptions, a total event-based load and yield for barium, cadmium, lead, and zinc for the events sampled were calculated for each water year (table 11). The total load and yield should be considered an estimate and a minimum representation of the total trace-element loads because limited data were available for the computations and not all events during the study period were sampled or had sufficient material mass for analyses.

All total loads and yields increased at each site for the four selected trace elements from the 2012 to the 2013 water years (table 11), most likely because of increased precipitation and runoff during the 2013 water year. The total barium load in suspended sediments was higher for sampled events collected at the downstream site during both study years, with the 2013 water year having the most substantial increase in total load from 29.4 tons at the upstream site to 69.6 tons at the downstream site. Cadmium load decreased during the 2012 water year from 0.105 tons at the upstream site to 0.029 tons at the downstream site and decreased slightly downstream during the 2013 water year from 0.433 tons at the upstream site to 0.344 tons at the downstream site. Lead loads slightly decreased during the 2012 water year from 7.02 tons at the upstream site to 6.37 tons at the downstream site, and only slightly increased downstream during the 2013 water year from 52 tons at the upstream site to about 68.7 tons at the downstream site. Zinc loads were lower at the downstream site than the upstream site, although the decrease in total load was not substantial during either water year (table 11). Comparison of the total yield of the four selected trace elements based on all events in each water year showed a decrease in barium, cadmium, lead, and zinc yields from the upstream to downstream site, indicating readily-available sediment sources are closer to the upstream site (table 11).

Seasonal comparisons of event-based loads and yields of lead and zinc concentrations in suspended sediments were similar between sites. The median loads and yields of lead and zinc were higher in spring at each site; however, the single winter event (event 4) at the downstream site had the highest median lead and zinc load during the study (fig. 14). Seasonal observation of the lead and zinc yields shows the single fall event (event 4) and the spring events at the upstream site have similar medians. Event-based loads and yields of lead and zinc in suspended sediments increased slightly from winter to spring at both sites and decreased greatly from spring to fall at the downstream site (fig. 14).



**Figure 14.** Seasonal comparison of stormflow-event loads and yields of lead and zinc in suspended sediments at two study sites on the Big River, Missouri, October 2011–September 2013.

## Summary

Missouri was the leading producer of lead in the United States—as well as the world—for more than a century. One of the lead sources is known as the Old Lead Belt, located in southeast Missouri. The primary ore mineral in the region is galena, which can be found both in surface deposits and underground as deep as 200 feet. More than 8.5 million tons of lead were produced from the Old Lead Belt before operations ceased in 1972. Although active lead mining has ended, the effects of mining activities still remain in the form of large mine waste piles on the landscape typically near tributaries and the main stem of the Big River, which drains the Old Lead Belt. Six large mine waste piles, some spanning more than a mile in diameter, exist within the Big River Basin. For the past century, the piles have been sources of lead and zinc-rich sediments to be transported by natural fluvial processes and wind downstream into the Big River. The U.S. Environmental Protection Agency (EPA) Region 7 completed 4-year reclamation efforts to cap and prevent further erosion of the piles in 2012.

A study was conducted by the U.S. Geological Survey in cooperation with EPA Region 7 to assess the amount and availability of suspended sediments and to assess the traceelement concentrations of suspended sediments transported through the Big River basin after reclamation of the mine waste piles. Streamflow and suspended sediments were quantified and sampled at two locations in the basin: Big River below Bonne Terre, Mo. (USGS site number 07017610; also referred to as the upstream site), located less than 5 miles downstream from the Old Lead Belt, and Big River near Byrnesville, Mo. (USGS site number 07018500; also referred to as the downstream site), located about 68 miles downstream from Bonne Terre. The Big River discharges into the Meramec River, which discharges into the Mississippi River, south of St. Louis, Mo.

Discrete suspended-sediment concentration (SSC) samples were used to develop a regression model with continuous turbidity measurements and (or) streamflow to compute time-series SSC and suspended-sediment load (SSL) values. Discrete SSC samples were paired with corresponding turbidity and streamflow measurements made at about the mean time of the SSC sample and plotted to identify outliers and trends.

The SSC, SSL, and sediment yields were computed for hydrologic events when cross-sectional sampling and streamflow measurements were collected. Seven events were sampled at the upstream site and six events were sampled at the downstream site during the study period.

Streamflows were greatest in the spring months and followed similar temporal variability at both sites. The maximum peak streamflow during the study period at the upstream site was 21,900 cubic feet per second (ft<sup>3</sup>/s) on April 19, 2013, and was 28,700 ft<sup>3</sup>/s on April 20, 2013 at the downstream site. Water temperature ranged from -0.1 to about 33 degrees Celsius (°C) at both sites. Turbidity ranged from 1.0 to 890 formazin nephelometric units (FNU).

Base-flow SSC values ranged from 1 to 74 milligram per liter (mg/L) at the upstream site during the study period, and event SSC values ranged from 74 to 1,091 mg/L. At the downstream site, base-flow SSC ranged from 4 to 127 mg/L and event SSC ranged from 27 to 871 mg/L. The upstream and downstream sites had similar SSC and SSL extremes during the study, but these extremes did not occur during the same events.

The annual SSL increased greatly during the study period, as the first water year (2012) was classified as a drought year and more precipitation was recorded during the 2013 water year. The upstream site had an annual SSL of 10,035 tons during the 2012 water year, and 191,294 tons for the 2013 water year. The downstream site had an annual SSL of 21,612 tons during the 2012 water year, and 333,717 tons for the 2013 water year.

An event-based average SSC and SSL were computed to help determine the mass of sediments transported during each sampled event. Event SSCs ranged from approximately 100 mg/L to 1,400 mg/L at both study sites and event SSLs ranged from about 180 to 32,000 tons at the upstream site, and from about 390 to 53,000 tons at the downstream site. Event SSLs were greatest at the downstream site. Event loads and yields were greater during water year 2013 events, with the April 2013 event having the greatest loads and yields at both sites.

Although a limited number of events could be sampled, using the continuous turbidity data to compute the daily SSL in conjunction with event sampling provided adequate data to determine the majority of the SSL in Big River occurs during stormflow events. Not all stormflow events that occurred during the study period could be sampled, yet the events that were sampled make up a considerable portion of the annual SSL. Discrete SSCs collected during base-flow conditions during the study period were generally very low (typically less than 50 mg/L). The base-flow average SSC was used with a median of daily median streamflow values to determine a base flow SSL. The base flow SSL at the upstream site was about 18 tons, or less than 0.01 percent of the SSL computed by the regression model during the study period. The event-based SSL from the seven sampled events during the study period was about 57,700 tons, accounting for about 29 percent of the SSL at the upstream site. At the downstream site, the computed base flow SSL was about 46 tons for the study period, which accounts for about 0.01 percent of the SSL, and the SSL from the six sampled events was about 103,000 tons, accounting for about 29 percent of the SSL computed by the regression model during the study period.

The total concentrations of barium, cadmium, lead, and zinc computed for each individual event sample were used to determine an event-based arithmetic average concentration to determine an event-based concentration, load (flux), and yield of each constituent. The arithmetic average trace-element concentrations were computed from all available samples during the designated event duration. For events with enough mass in both the sand and fines fraction for analysis, it was noted that nearly all sand fraction concentrations were less than the concentrations of the fines fraction for all four trace elements. Barium concentrations were nearly twice as high in event samples collected at the downstream site as compared to samples from the upstream site. The likely source of barium in the Big River is the Mineral Fork and Mill Creek, which flow through the historical barite (barium sulfate, also known as tiff) mining district in Washington County. Cadmium and zinc concentrations were nearly two times higher at the upstream site than at the downstream site, while lead concentrations appeared similar between both sites. It is possible the suspended sediments containing cadmium, lead, and zinc have decreased concentrations downstream because slower velocities cause the sediments to fall from suspension as they are transported downstream farther from their source. Traceelement concentrations in suspended sediment sampled during stormflow events during a previous study had higher concentrations of lead and zinc than concentrations measured in suspended sediments collected during events at the upstream site. Although the previous study concentrations were higher (1,100 to 3,200 milligram per kilogram [mg/kg] of lead; 1,100 to 2,200 mg/kg of zinc) than those measured at the upstream site (680 to 1,400 mg/kg of lead; 470 to 1,200 mg/kg of zinc), there are no indications of long-term or substantial decreases as data are limited and could be affected by differences in sampling location, event intensity, changes in the geomorphology of the stream, or remediation efforts of mine waste piles.

Sediment quality guidelines for freshwater describe two qualities of environmental effects from trace-element concentrations in suspended sediments-the threshold effect concentration (TEC) and the probable effect concentration (PEC)and help regulatory agencies assess the toxicity of sediments within a remediation study. Concentrations of cadmium, lead, and zinc in suspended sediment samples collected during stormflow events at both sites exceeded the consensus-based TEC and consensus-based PEC. All lead and zinc concentrations in the fine fraction of all suspended sediment from both sites greatly exceeded the consensus-based TEC (35.8 mg/kg for lead; 121 mg/kg for zinc) and the PEC (128 mg/kg for lead; 459 mg/kg for zinc). Lead concentrations in the fine fraction of all samples at both sites also exceeded the toxic effect threshold (TET) of 170 mg/kg, above which sediment is considered to be heavily polluted causing adverse effects on sediment-dwelling organisms. Zinc concentrations in the fine fraction in four of five sampled events from the upstream site also exceeded the TET of 540 mg/kg.

Concentrations of cadmium and zinc were notably higher in suspended sediment samples from the upstream site compared to the downstream site, especially in the fine fraction. The smaller cadmium and zinc concentrations at Summary 37

the downstream site could be a result of a decrease in source material enriched in these trace elements in the downstream areas of the watershed compared to the upstream area within the Old Lead Belt. The lead concentrations greatly exceeded the PEC as well as the TET, in some samples by a factor of 10, which indicates that lead-rich suspended sediments, especially in the fine fraction, are readily available for transport within the Big River Basin. These lead-enriched, finer sediments could remain in the system from historical mining, and as the capping of mine waste piles upstream from Bonne Terre continues to reduce additional sediment loadings, these fine sediments may be continually released as the river scours the streambed and erodes the stream banks, causing lead-rich suspended sediment to remain in a state of equilibrium.

Event-based trace-element load and yields in suspended sediments also were used for analyses of sediment quality in the Big River. The total barium load in suspended sediments was higher for sampled events collected at the downstream site during both study years. Cadmium and zinc loads in suspended sediments were lower at the downstream site than the upstream site, although the decrease in total load was not substantial during the study period. Lead loads in suspended sediments were lower at the downstream site during the first study year, with a slightly higher load downstream in the second year though the increase from upstream to downstream was small. Event yields were higher at the upstream site. Storm events at the downstream site had much longer durations and lower velocities than events at the upstream site. All four trace element total loads and yields in suspended sediments computed from event samples increased at each site from the 2012 to the 2013 water years, most likely because of increased precipitation and runoff during the 2013 water year. Total loads of barium, cadmium, and lead were higher at the downstream site than the upstream site during both water years. Comparison of the total yield of the four selected trace elements based on all events in each water year showed a decrease in barium, cadmium, lead, and zinc yields from the upstream to downstream site, indicating readily-available sediment sources are closer to the upstream site.

Median lead and zinc concentrations collected in spring were similar at both sites, whereas median concentrations of lead and zinc were greatest in fall at the upstream site and greatest in winter at the downstream site. It is possible that the median concentrations in the fall were greater at the upstream site because of one large event in September 2012. The winter event at the downstream site occurred in January 2013, after the removal of vegetation from the banks near the streamgage location, which could have increased the available suspended sediments during runoff. Seasonal comparison of event-based loads computed at the upstream site were largest for all four constituents during April 2013 (event 7), with the lead load being the largest with 29.4 tons transported during the event.

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Publishing support provided by: Rolla Publishing Service Center

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