Legacy sediment, lead, and zinc storage in channel and floodplain deposits of the Big River, Old Lead Belt Mining District, Missouri, USA

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A B S T R A C T

The Old Lead Belt of southeastern Missouri was one of the leading producers of Pb ore for more than a century (1869–1972). Large quantities of contaminated mine waste have been, and continue to be, supplied to local streams. This study assessed the magnitude and spatial distribution of mining-contaminated legacy sediment stored in channel and floodplain deposits of the Big River in the Ozark Highlands of southeastern Missouri. Although metal concentrations decline downstream from the mine sources, the channel and floodplain sediments are contaminated above background levels with Pb and Zn along its entire 171-km length below the mine sources. Mean concentrations in floodplain cores ~2000 mg kg⁻¹ for Pb and ~1000 mg kg⁻¹ for Zn extend 40–50 km downstream from the mining area in association with the supply of fine tailings particles that were easily dispersed downstream in the suspended load. Mean concentrations in channel bed and bar sediments ranging from 1400 to 1700 mg kg⁻¹ for Pb extend 30 km below the mines, while Zn concentrations of 1000–3000 mg kg⁻¹ extend 20 km downstream. Coarse dolomite fragments in the 2–16 mm channel sediment fraction provide significant storage of Pb and Zn, representing 13–20% of the bulk sediment storage mass in the channel and can contain concentrations of >4000 mg kg⁻¹ for Pb and >1000 mg kg⁻¹ for Zn. These coarse tailings have been transported a maximum distance of only about 30 km from the source over a period of 120 years for an average of about 250 m/y. About 37% of the Pb and 9% of the Zn that was originally released to the watershed in tailings waste is still stored in the Big River. A total of ~157 million Mg of contaminated sediment is stored along the Big River, with 92% of it located in floodplain deposits that are typically contaminated to depths of 1.5–3.5 m. These contaminated sediments store a total of 188,549 Mg of Pb and 34,299 Mg of Zn, of which 98% of the Pb and 95% of the Zn are stored in floodplain deposits. Most of the metal mass in channel deposits is stored near the mines, with 72% of the Pb and 78% of the Zn occurring in the 25 km of channel proximal to the mine source. Although environmental assessments of streams contaminated by mines often focus on evaluating metal concentrations in the geochemically active fine sediment fractions, about 60% of the Pb stored in channels is associated with coarse dolomite tailings fragments deposited in channels within 25 km of the mines. The magnitude and widespread distribution of Pb and Zn storage in legacy floodplain sediments ensures that remobilization by bank erosion will be a continuing problem for water quality far into the future.

1. Introduction

In 1864, George Perkins Marsh explained how forest clearing and soil erosion produced flooding, channel change, and sedimentation along rivers and coasts in the Old World and North America, even quoting Pliny the Elder who reported similar observations in the first century A.D. (Lowenthal, 1965). Now widely acknowledged, human activities are responsible for modifying the geomorphic characteristics of river systems worldwide, often with negative consequences for the economy and population (Kondolf, 1997; Wilkinson and McElroy, 2007; Hoffmann et al., 2010; UNESCO, 2011). Moreover, significant costs are often attributed to human-induced soil erosion and resulting impacts on sedimentation in river channels and on floodplains, including long-term sediment storage that can degrade watershed functions (Walling, 1983, 1999; Slaymaker, 2003; de Vente et al., 2007). In North America alone, physical, chemical, and biological damage from sediment problems may currently exceed $24 billion annually (Osterkamp et al., 1998; dollars adjusted for inflation). Legacy sediment is a recognized cause of geomorphic and water quality problems in watersheds; it is generated by widespread and/or intensive episodes of anthropogenic disturbances such as initial settlement and land and population (Kondolf, 1997; Wilkinson and McElroy, 2007; Hoffmann et al., 2010; UNESCO, 2011). Moreover, significant costs are often attributed to human-induced soil erosion and resulting impacts on sedimentation in river channels and on floodplains, including long-term sediment storage that can degrade watershed functions (Walling, 1983, 1999; Slaymaker, 2003; de Vente et al., 2007). In North America alone, physical, chemical, and biological damage from sediment problems may currently exceed $24 billion annually (Osterkamp et al., 1998; dollars adjusted for inflation). Legacy sediment is a recognized cause of geomorphic and water quality problems in watersheds; it is generated by widespread and/or intensive episodes of anthropogenic disturbances such as initial settlement and land
clearing, expansion of row crop and timber agriculture, grazing, and urbanization (James, 2013). Legacy sediment commonly occurs in river valleys as post-settlement alluvium on floodplains or colluvium along slope margins and contains some properties of human origin such as industrial and mining wastes or disturbed soil texture and mineralogy.

Although legacy was not yet used to describe historical alluvial deposits, geomorphological studies of legacy sediments and related watershed processes generally began in North America in the 1970s, most notably in the upper Midwest and southeastern Piedmont regions of the USA (Knox, 1972; Trimble, 1974, 1983; Magilligan, 1985; Jacobson and Coleman, 1986; Phillips, 1991; Beach, 1994; Bettis and Mandel, 2002; Wilkinson and McElroy, 2007; Walter and Merritts, 2008). These works were based on earlier efforts to understand relationships between soil erosion and stream channel and floodplain sedimentation (e.g., Happ et al., 1940; Wolman, 1967). However, G.K. Gilbert's (1917) classic study of hydraulic gold mining in the Sierra Nevada of California and its influence on excessive sediment loads in rivers downstream was one of the first to quantify the fluvial response to episodic inputs of legacy sediment and to develop a watershed-scale sediment budget (James, 1989, 2010; James and Lecce, 2013). Gilbert's work showed that the production, transport, and storage of legacy sediment is a nonequilibrium process, characterized by temporal lags and intermittent movement of sediment through the system (James et al., 2017).

Alluvial floodplains can function as important storage locations for legacy sediment and for associated metal contaminants in watersheds affected by mining (Davies and Lewin, 1974; Macklin, 1985; Knox, 1987; Bradley, 1989; Moore and Luoma, 1990). In some cases, the volume of mining sediment can overwhelm the river and exceed its ability to transport the imposed load, causing manifest changes in channel morphology (James, 1989; Knighton, 1989). On the other hand, sediment discharges from mining sites may originate from a limited number of mine sources within a watershed and therefore only interfere with geomorphic processes locally. Importantly, mining sediment inputs composed of mill tailings from mineral processing can contaminate channel and floodplain deposits with metals such as lead (Pb) and zinc (Zn) for distances of several hundred kilometers downstream and to concentrations exceeding 5000 mg kg\(^{-1}\) (Ritcey, 1989; Horowitz, 1991; Miller and Orbock Miller, 2007). During the period of mining, >40% of the tailings introduced into a river system may become stored in floodplain deposits (Jeffery et al., 1988; Marron, 1989, 1992). However, after mine closure, subsequent remobilization of stored mining sediment by bank erosion and weathering can continue to contaminate the river for centuries (Ongley, 1987; Leenaers, 1989; Coulthard and Macklin, 2003; Lecce and Pavlowsky, 1997; Lecce et al., 2008). Indeed, Hudson-Edwards et al. (1999) showed that floodplains contain a 2000-year record of mining contamination in northeast England. Consequently, geochemical profiles in mining-contaminated floodplains can be used as a stratigraphic tracer to more precisely identify and date legacy deposits (Macklin, 1985; Knox, 1987; Lecce and Pavlowsky, 2001, 2014; Bain and Brush, 2005). As with legacy sediment in general, mining sediment and contaminant storage in watersheds is inherently controlled in large part by geomorphic and sediment transport factors (Bradley and Cox, 1990; Graf et al., 1991; Graf, 1994, 1996; Ciszewski and Matys Grygar, 2016).

The Big River (2500 km\(^2\)) drains the Old Lead Belt mining district (OLB), which covers 280 km\(^2\) of St. Francois County in southeastern Missouri with its center about 100 km south of St. Louis (Figs. 1 and 2). The OLB was a leading producer of Pb worldwide from 1869 to 1972, ranking first in USA production for all years except one since 1908 (Buckley, 1909; Minerals Yearbook, 1972). During this century-long period of intensive mining, large volumes of tailings containing high concentrations of Pb and other metals such as Zn, copper (Cu), and cadmium (Cd) were released into nearby streams, including the Big River (Fig. 3). Even after the last mine closed in 1972, tailings materials stored in six large abandoned piles, each covering > 1 km\(^2\), were still entering waterways through gully erosion, slope failures, and dam breaches (Mosby et al., 2009). A decade or two after cessation of mining activities, several studies confirmed the degree of metal contamination in channel sediments in the Big River near the mining sites in St. Francois County, Missouri (Schmitt and Finger, 1982; Davies and Wixson, 1987; Smith and Schumacher, 1991, 1993) and the potential influence on aquatic life (Gale et al., 2002, 2004). Designated as Superfund sites, the major tailings piles and slime ponds in the district were stabilized between 1994 and 2016 by U.S. Environmental Protection Agency-Region 7 (USEPA, 2017a) (Fig. 4). However, large volumes of metal-contaminated sediment are still stored in bed and bar deposits within the main channel below mining sites (MDNR, 2001, 2003). These mining sediments pose a long-term environmental risk the deposits are available for reworking, downstream transport, and geochemical release of toxic metals to the river system (Alesandrini, 2014). Moreover, the contribution of contaminated legacy deposits on floodplains to total contaminant storage along the Big River has not yet been evaluated.

Presently, major concerns persist over the longer-term effects of sediment contamination and excess mining sediment load on geomorphologic processes, ecological impacts (including freshwater fish and endangered mussels), the community economy, and human health in the Big River watershed (Murray, 1926; MDNR, 2007b; Roberts et al., 2009; Hinck et al., 2012; Alesandrini, 2014). Understanding the geomorphic dimensions and contaminant distribution of metal storage in the Big River is paramount to addressing these problems. Previous studies identified elevated Pb and Zn concentrations in present-day channel sediments of the Big River (Schmitt and Finger, 1982; Smith and Schumacher, 1991, 1993; Gale et al., 2002, 2004; Roberts et al., 2009); however, the magnitude and spatial distribution of contaminated sediment in active channel and floodplain deposits at the reach and segment scales have not been quantified. Besides the environmental problems posed by historical mining (Mosby et al., 2009; Alesandrini, 2014), an examination of the interconnections among the mining history, contaminated sediment patterns, and storage volumes of channel and legacy floodplain deposits offers the opportunity to better understand where and how sediment storages form and change over time (Ottesen et al., 1989; Graf, 1994, 1996; Walling et al., 2003; Macklin et al., 2006). Further, more information is needed overall to understand how sediment contaminant budgets can be used to interpret fluvial processes and alluvial history in medium- to large-sized watersheds (Meade, 1982; Slaymaker, 2003; Hoffmann et al., 2010).

The purpose of this paper, therefore, is to assess the magnitude and spatial distribution of mining-contaminated sediment stored in the main channel and adjacent floodplain of the Big River. In particular, we focus on quantifying downstream trends in reach-scale bed and bar storage, developing landform relationships for contaminated channel deposits and floodplain soils, and comparing downstream storage trends for coarse and fine sediment fractions. Previous efforts to understand contaminated sediment and metal storage in the watershed have informed the present study, but were unable to consider the spatial complexity of sediment storage in Big River. These studies focused on understanding channel sediment-metal variability within a single reach (MDNR, 2001, 2003), tailings pile volume and composition (Newfields, 2006), localized channel storage volume at sites immediately below mine input points (Newfields, 2007), and patterns of channel bar storage (MDNR, 2007a; Wang et al., 2016). This study applies a geomorphological sediment/metal budget approach (e.g., Macklin et al., 2006; Dennis et al., 2009) to quantify and interpret present-day channel and floodplain storage trends of metal contaminants and their relationship to historical mining and legacy sedimentation along 171 km of Big River from Leadwood to its confluence with the Meramec River near Eureka, Missouri.

2. Study area

Big River drains the Ozark Highlands (level III) ecoregion in Missouri including portions of St. Francois Knobs and Basins, Meramec River Hills,
and Eastern Ozark Border (level IV) subregions (USEPA, 2017b). The headwaters of the river originate at 485 m amsl on metagneous rocks of the St. Francois Mountains and the watershed drains a well-dissected landscape with narrow divides and a basin relief of 300 m. Most of the drainage area of the Big River, including the OLB, is underlain by horizontally bedded dolomite with some limestone, shale, and sandstone units (Meneau, 1997). The major ore mineral in the OLB is galena (Pb-sulfide) with a secondary abundance of sphalerite (Zn-sulfide), some smithsonite (Zn carbonate), and other less valuable sulfide minerals (Smith and Schumacher, 1993). Mineralization typically occurs in the Bonne Terre Dolomite of Cambrian age at a depth of 60–300 m but outcrops at the surface in places in the southern and eastern portions of the basin. Large ore bodies were typically over 240 m wide, 360 m long, and 60 m in thickness with some worked continuously for several kilometers (Jackson et al., 1935).

Pleistocene glaciers did not reach the Big River watershed, but ice margins were close, being located about 20 km to the north of the mouth (R-km 0) along the Missouri River and 20 km to the east of the

![Fig. 1. Big River watershed, Missouri.](image-url)
main valley along the Mississippi River (Rovey and Balco, 2011). Upland soils are typically formed in a thin layer of silty Pleistocene loess overlying cherty or noncherty residuum formed in dolomite, limestone, and shale (Brown, 1981; Skaer, 2000; Skaer and Cook, 2005). The climate is moist continental with an average annual temperature of about 13 °C ranging from an average of 0 °C in January to 25 °C in July. The mean annual rainfall is about 102 cm with the wettest period in the spring months (Brown, 1981). The U.S. Geological Survey discharge gaging station (Big River at Byrnesville, MO, #07018500) has a drainage area of 2375 km² with a mean flow of 25 m³/s since 1921. The flood peak of record occurred on 25 September 1993 at a stage of 9 m and discharge of 180 m³/s. Land use in 2006 in the Big River watershed was 72% forest, 18% grassland, 1% rowcrops, and 7% urban/developed; and population in the 2010 census was 98,252 persons (MDNR, 2013).

2.1. Mining history

Southeastern Missouri has a long mining history beginning in 1720 by French explorers at Mine-La-Mott near Fredricktown located about 40 km southeast of the OLB (Seegeer, 2008). Lead was probably first mined in the Big River watershed between 1742 and 1762 near Potosi where relatively large galena crystals were extracted by hand from shallow pits or diggings (Buckley, 1909). The U.S. Bureau of Mine records indicate that these crude mining practices continued sporadically until the 1940s, contributing <2% of the total Pb produced by the OLB (Buckley, 1909). The first organized mining operations in the OLB began about 1864 in Bonne Terre; and large-scale, deep shaft mining began as mining spread to the nearby towns of Leadwood, Desloge, and Flat River in the 1890s. Annual metallic Pb production rose rapidly after 1907 with years of peak production in 1917, 1925, and 1942 and decreased production in the early 1930s during the Great Depression. When the last mine closed in 1972, it was reported that about 9 million Mg of Pb and 1.8 million Mg of Zn metal had been produced in the Old Lead Belt (Mineral Yearbook, 1972).

Fig. 2. Big River channel in the mining area. A at R-km 156.1 and B at R-km 147.

2.2. Mining sediment and metal inputs

As compiled from Bureau of Mining annual reports of Mineral Resources of the U.S. and the Mining Yearbook, mining discharged about 264 million Mg of mine tailings wastes to nearby streams, flat land areas, or constructed ponds from 1866 to 1972 in the Big River watershed (Jackson et al., 1935). Up to six major mining sites operated in the OLB for periods ranging from 33 to 84 years with a combined mill capacity of 24,000 Mg of ore per day at the peak in 1933. Presently, abandoned tailings piles cover over 11 km² and about 57 million Mg of tailings were removed by rail for road ballast or fertilizer, used locally for agriculture, or constructed ponds from 1866 to 1972 in the Big River today as dark gray dolomite fragments in the fine gravel fraction of bed and bar deposits below mining areas (Fig. 6). Chat tailings typically contained 3000–5000 mg kg⁻¹ Pb (Jackson et al., 1935).

Gravity concentration using wet shaking table methods created tailings with >75% in the fine to medium sand range (0.125 to 0.5 mm). Coarse chat tailings with 75% in the 4–8 mm size fraction were generated by dry and wet jiggling using sieve boxes and sluices until around 1930 when better table and flotation methods were introduced (Wright, 1918; Jackson, 1929; Newfields, 2006) (Fig. 5). While stored in large chat dumps or piles around the district (USFWS and MDNR, 2007), chat tailings are easily identifiable in the Big River today as dark gray dolomite fragments in the fine gravel fraction of bed and bar deposits below mining areas (Fig. 6). Chat tailings typically contained 3000–5000 mg kg⁻¹ Pb (Jackson et al., 1935).

2.3. Texture of the mining sediment

The grain size characteristics of tailings materials influence the ability of fluval processes to transport contaminated sediment downstream, with finer particles being transported downstream or on floodplains at higher rates compared to coarser particles (Ritcey, 1989). In the OLB, crude ore was crushed and ground to specific sizes to improve the recovery of galena by gravity concentration owing to higher particle density and froth flotation using chemical treatments to float and concentrate sulfide particles. Mill wastes in the OLB can be generally classified into three different types: coarse chat, fine tailings, and slimes (Jackson, 1929; Coghill and O’Meara, 1932; Jackson et al., 1935).

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Gravity concentration using wet shaking table methods created tailings with >75% in the fine to medium sand range (0.125 to 0.5 mm). Vibrating shaking tables used hydraulic force to separate the ore particles into concentrate for the smelter, middlings for reprocessing, and tailings for the dump pile or further grinding for flotation treatment based on density differences (Taggart, 1945). Gray and tan sand grains from mining sources are still relatively abundant in channel deposits today. Because of more efficient treatment of the finer feed, tailings from shaking tables typically contained <1200 mg kg⁻¹ Pb (Coghill and O’Meara, 1932).

Flotation circuits produced very fine tailings, sometimes referred to as slimes, with 66% in the silt and clay size range (~0.074 mm). Froth flotation was introduced in 1914 to improve Pb extraction from the finely-disseminated ores common to the OLB. Using chemical reagents to bind air bubbles to sulfide particles, rich ore particles were floated to the top of the tank and skimmed off as valuable concentrate (Jackson et al., 1935). Flotation tailings were usually mixed and slurried with gravity mill wastes and then discharged to large tailings or slime ponds near the mill. In general, ultrafine particles such as slimes were difficult to manage in concentration mill circuits (i.e., Taggart, 1945; Somasundaran, 1986) with possibly 1–6% of the total tailings mass being discharged as slimes to tailings ponds or local streams in overflow and other mill effluents (Buckley, 1909; Wright, 1918; Jackson et al., 1935). Metal values in overflow slime particles could not be recovered and so they contained high Pb concentrations reflecting the grade of untreated ore. Ore grade in the Big River watershed averaged 27,000 mg kg⁻¹ Pb between 1894 and 1972 and up to 60,000 mg kg⁻¹ Pb before rich ore bodies were depleted prior to 1930 (Jackson et al., 1935).
2.4. Geomorphic significance

While the majority of the tailings piles in the subdistrict have had some level of stabilization that has reduced or contained erosion, questions still remain about the fate of the materials presently in transit in the channel system or temporarily stored in floodplain deposits. A preliminary assessment of the storage of mining chat and tailings estimated that 1,600,000 Mg was stored in channel deposits of the Big River below the mines and 19,000 Mg in Flat River Creek (Newfields, 2007). However, floodplain deposits have the potential to store larger volumes of contaminated sediment compared to channel deposits in the Big River. For example, the floodplain area available for sediment deposition along the Big River is about six times greater than for the river channel. Moreover, compared to higher energy channel bed conditions, overbank floodplain deposits have the potential to store more fine-grained sediment including sand- and slime-sized tailings that typically have higher metal concentrations (Bradley, 1989; Bradley and Cox, 1990).

Fig. 5. Tailings at the National Pile in 2008. Note angular fine gravel-sized chat (2–16 mm) with finer matrix.

Fig. 6. Channel Bar with blue gray dolomite “chat” fragments at R-km 140.6. Chat sediment particles are more sub-angular and rounded compared to those in the tailings pile and represent from 15 to 25% of the bulk channel sediment at this location.
Besides the greater capacity for fine sediment storage in floodplains, the supply of sediment available for storage in legacy floodplain deposits may have been enhanced by land use changes in the watershed. Agricultural settlement and timber harvesting resulted in widespread hydrological changes in the Ozark Highlands between 1880 and 1930 (Jacobson and Primm, 1994). Indeed, land use factors resulted in increased runoff, soil erosion, and channel incision in headwater catchments, increases in flood frequency, and deposition of sand and gravel bars in main channels (Jacobson, 1995; Martin and Pavlowsky, 2011). Coincidentally, these activities overlapped with a period of productive mining in the OLH when relatively crude and inefficient milling and tailings disposal practices were in use (Jackson, 1929; Coghill and O’Meara, 1932; Jackson et al., 1935). Even during low flow conditions, tributary streams and downstream river channels were filled with gray suspended sediment (slimes) released from mining operations (Buckley, 1909). Therefore, the excess supply of contaminated fine sediment in Big River suggests that floodplain storage rates of historical mining sediment would be relatively high. Indeed, increased rates of overbank sedimentation on river floodplains during the early twentieth century have been reported in other Ozarks watersheds (Owen et al., 2011).

3. Methods

Study site locations are described along the main stem of the Big River using the river-kilometer (R-km) where R-km 0 is located at the mouth of the Big River at the confluence with the Meramec River and R-km 171 is at the most upstream limit of mining inputs at the confluence of Eaton Branch (which drained the Leadwood Mine) (Fig. 1). To evaluate downstream trends in channel geomorphology and storage, channel characteristics were characterized for 10 different valley segments delimited based on the locations of mine sources and tributary confluence points (Table 1). Segment lengths average 17.1 km and range from 12 to 26.5 km (270–490 channel widths).

3.1. Field data collection

3.1.1. Geomorphic assessment of channel storage

A storage volume assessment including geomorphic analyses and sediment characterization was completed at 10 sampling reaches along the main stem of the Big River. The sampling reaches typically range in length from 10 to 12 channel widths and are different than the much longer valley segments described in the previous section. Topographic channel surveys were used to determine channel dimensions, the height of banks or floodplain surfaces, and minimum/maximum depths of potential mining sediment. Along each reach, 9 or 10 channel cross sections spaced at intervals of one channel width were used to measure channel capacity and to quantify channel bar and bed deposits. The center of each sample reach was located within a glide channel unit just above a riffle crest except at three sites where low water bridges or dams affected the character of the river. We surveyed the longitudinal profile along the channel thalweg of each reach to determine the location of pools, riffles, and glides (Panfil and Jacobson, 2001). Surveys were conducted with an electronic total station or auto level and georeferenced with at least two submeter resolution global positioning system (GPS) points.

We estimated the total thickness of sand and fine gravel sediment stored in the channel using the maximum refusal depth with a tile probe at 5–10 locations across each active channel cross section (similar to Newfields, 2007). This is a quick but reliable method because the tile probe can easily penetrate the sand and fine gravel deposits formed by the mixture of mine tailings and mobile natural bed materials but cannot penetrate the coarse bed substrates, now buried, that formed the channel boundary prior to historical disturbances (Jacobson and Primm, 1994). As discussed later, given the high number of probe points collected and typically shallow depths to bedrock in Ozark rivers, we believe that probe depth measurements are relatively accurate indicators of stored historical and recent sediment in channel bar and bed deposits in the Big River (Newfields, 2007).

3.1.2. Channel sediment sampling

Channel sediments were sampled at sites located along the main stem from above the most upstream mine at Leadwood (R-km 171) to the mouth of the Big River (R-km 0) near bridge crossings, public access areas, or by boat at intervals of <1 to 20 km. Most sites were sampled in 2009 (24), but additional sites were collected in 2010 (3) and 2011 (1). Two control sites located above mining influence were included at R-km 192 and 181. A total of 216 channel bed and bar samples were collected for geochemical analysis at 28 sampling sites. Channel bar and bed deposits were sampled separately to evaluate sediment texture and geochemistry. Where exposed above the water line during low flow conditions, bars were sampled from shallow pits by shovel at a depth of approximately three times the maximum clast size observed on the bar surface to exclude the influence of surface arming on sediment measurements (Bunte and Abt, 2001) (Fig. 7). Typically, three samples were collected from a given bar deposit at a depth of 10–20 cm along the centerline of each bar at the head, middle, and tail locations. Samples were collected by hand or plastic trowel from heaped material contained on the shovel blade which was never in contact with metal. Where possible, at least two different bar features were sampled within each reach. Beds were usually sampled in about 0.5 m of water at glide units where flow shallows and spreads out at the tail end of a pool prior

Table 1

Channel width and bar areas by river segment.

<table>
<thead>
<tr>
<th>Segment number</th>
<th>Tributary</th>
<th>R-km</th>
<th>Drainage area (km²)</th>
<th>Length (km)</th>
<th>Avg. active width (m)</th>
<th>Avg. bed width (m)</th>
<th>Bar width (m)</th>
<th>% total</th>
<th>Channel length lacking bars %</th>
<th>Channel length with &gt;50% bars</th>
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<tbody>
<tr>
<td>1</td>
<td>Eaton Branch at Leadwood</td>
<td>171</td>
<td>12</td>
<td>16</td>
<td>43.1</td>
<td>29.9</td>
<td>13.2</td>
<td>31</td>
<td>18</td>
<td>48</td>
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<td>2</td>
<td>Flat River Creek</td>
<td>155</td>
<td>137</td>
<td>10.5</td>
<td>35.7</td>
<td>27.5</td>
<td>8.2</td>
<td>23</td>
<td>25</td>
<td>45</td>
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<td>3</td>
<td>Terre Beau Creek</td>
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<td>16.5</td>
<td>42.5</td>
<td>34.8</td>
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a Tributary input at upstream boundary of river segment.
b Upstream boundary of river segment.
c Big River drainage area is 626 km² at R-km 171.25 and 2500 km² at mouth.
d Percentage of the segment length where bars cover >50% of the channel area.
to crossing a riffle crest or from a relatively featureless plane bed indicative of local aggradation (Panfil and Jacobson, 2001). Glide deposits were collected by pushing a small plastic bucket into the bed (after removing any armor layer) to obtain a subaqueous core of bed sediment to a depth of 15–20 cm (Fig. 7). The sample was dewatered by decantation before storing in a plastic bag. Up to three samples were collected at even spacing across each glide unit perpendicular to flow and up to three glides were tested at each sampling site.

3.1.3. Floodplain sediment sampling

We sampled geochemical profiles at 68 different points on floodplains along the Big River, including 35 cut-bank exposures by hand and 33 coring sites using a truck-mounted Giddings rig. A total of 502 individual samples were collected for Pb and Zn analysis. For bank sampling, typically 3–6 depth-integrated samples were collected down each cutbank at intervals based on observed stratigraphic units and apparent mining influence. Giddings cores were collected along several cross-valley transects to check for vertical and lateral variations in contaminated depth of the floodplain deposit to background threshold concentrations. Typically 8–13 depth increments were sampled from each core. For bank and core sampling, samples were collected with a trowel, bagged, and treated similarly as the channel samples. At most sites at least two different floodplain units were sampled, including one from the recent bankfull floodplain surface and the other from a younger bench feature typically 0.5–1 m lower and <10 m wide as determined in the field or located on soil maps (Brown, 1981; Royall et al., 2010). In some reaches, multiple bench, floodplain, and terrace surfaces were sampled.

Fig. 7. Channel deposits sampled for this study. A-Glide entering riffle at R-km 156.9. B-Large alternate bar at R-km 156.4.
3.2. Laboratory methods

All laboratory work was carried out by Ozarks Environmental and Water Resources Institute (OEWRI) staff at Missouri State University. Standard operating procedures can be found at http://oewri.missouristate.edu/.

3.2.1. Sample preparation and textural analysis

All channel and floodplain sediment samples were hand sieved to determine the particle size distribution and to isolate size fractions for further analysis. Samples were dried in an oven at 60 °C, disaggregated with mortar and pestle, and passed through a sieve set to separate the <2 mm and fine gravel fractions for further analysis of the <64 mm bulk sediment fraction. Larger clasts (>64 mm) were excluded from analysis because they were too large for the sampling procedures being used, rarely originate from mining sources (Jackson et al., 1935; Taggart, 1945), add increased variability to being used, and standard hot acid extraction methods (USEPA, 1998). Selected samples were split sampled in the laboratory and sent to a commercial laboratory for metal extraction using hot nitric and hydrochloric acids (i.e., aqua regia) and analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The ratio of aqua regia over XRF concentrations was used to convert sediment XRF results to equivalent aqua regia concentrations. Thirteen channel bar samples from the Big River in St. Francois County yielded median aqua regia:XRF values and average quartile ranges as follows: Pb, 1.09 ± 37% and Zn, 1.27 ± 25%. Fifteen floodplain soil samples from the Big River in St. Francois County yielded median aqua regia:XRF values and quartile ranges as follows: Pb, 0.82 ± 5% and Zn, 0.88 ± 4%. The XRF concentrations were multiplied by the representative median ratio values to determine corrected aqua regia values that were used to calculate storage budgets. Using the ratio approach, metal concentrations are adjusted uniformly but maintain the original site and sample variability as measured by XRF. This correction is also relevant for environmental risk assessment as Pb concentrations determined by aqua regia extraction from road dusts and soils in mining areas in southeastern Missouri near the present study area were significantly correlated with geochemical mobility and digestive uptake by humans (Witt et al., 2014).

3.2.4. Bulk and particle density

The bulk density values for channel and floodplain deposits were needed to convert sediment volume measurements to mass units for sediment and metal storage calculations (Dennis et al., 2009). Bulk density values for sand and fine gravel deposits and porous sandstones typically range from 1.9 to 2.2 Mg/m³ (Manger, 1963). Therefore, after also reviewing several tables used by geotechnical engineers and excavation contractors, a value of 1.92 Mg/m³ was selected to estimate bulk density of the <2 mm sediment fraction in channel deposits. A value of 2.2 Mg/m³ was selected to apply to the 2–64 mm mixed gravel fraction (Bunte and Abt, 2001). The particle density of pure dolomite averages 2.84 Mg/m³ and several samples of the Bonne Terre dolomite averaged 2.66 Mg/m³ (Manger, 1963). Soils formed in fine-grained overbank floodplain deposits along the Big River typically have bulk density values of 1.5 Mg/m³ (Brown, 1981).

3.3. Channel and floodplain feature classification

Geospatial data for the Big River were acquired from ArcGIS®, collected in the field with survey equipment, and georeferenced or downloaded from the Missouri Spatial Data Information Service (MSDIS). Channel bar and bed features were manually digitized based on the interpretation of 2013 aerial photographs with submeter resolution (Fig. 8). Active channel width was measured between opposite lower bank lines identified by the water surface contact or bar margin including the wetted channel bed and, when present, all subaerial bar deposits. To the extent possible, active (unvegetated) or vegetated bar features were delineated along the low-flow waterline and bank margin. Channel dimensions were averaged within 500-m-long polygons or cells along the river-kilometer centerline.

The SSURGO database provided by the Natural Resources Conservation Service was used to delineate floodplain areas along the valley floor of the Big River. Digital copies of the soil surveys were published in 2006 representing soil field work completed during the calendar years as follows: Jefferson County, 2000; St. Francois County, 1974–1976; and Washington County, 2002. Only those floodplain features assumed to have formed or received sediment since the beginning of the mining period to present were included in this analysis. Therefore, only soil series classified as flooding once or more every two years (i.e., frequent flooding) were used to determine overbank floodplain areas. To verify floodplain areas, SSURGO layers were compared to digital elevation models (DEMs) and aerial photographs. We also used the elevation and apparent age of floodplain features during our field studies to verify geomorphic relationships of the mapped...
soil units. The four soil series used to delineate floodplain area and width for the Big River were: (i) Sturkie series on low terraces; (ii) Haymond series on well-drained floodplains; (iii) Wilbur series in low-lying floodplain areas such as a back-swamp or swale; and (iv) Kaintuck series on recent or incipient floodplain deposits, or bench features (Brown, 1981).

3.4. Storage budget calculations

Sediment and metal storage budgets were calculated from field and laboratory measurements including: (i) channel and floodplain area and depth of the deposit; (ii) bulk density of the deposit to convert volume to mass; and (iii) mean metal concentrations within the deposit to determine mining-metal mass storage (Dennis et al., 2009; Lecce and Pavlowsky, 2014). In addition to the above, the textural composition of the deposit is often applied in calculations because specific size fractions may disproportionately contain either more or less of the contaminant or be distributed differently among different deposits (Graf, 1994). To remove the influence of naturally occurring metals on the contamination budget, the mining metal concentration was used in contaminated metal storage calculations and was determined as the total metal concentration minus the expected background or premining concentration. For channel sediment, only the <2 mm sediment fraction and 2–16 mm dolomitic chat fragment fraction contributed to contamination, while the rest of the 2–64 mm fraction was considered to add no mining metal mass to the sediment. For floodplain sediment, only the <2 mm sediment fraction contributes to contamination because the content of dolomite fragments in overbank deposits is negligible.

4. Results

4.1. Channel storage

4.1.1. Channel bed and bar volumes

Digitized channel bed and bar areas from 2013 aerial photographs were used to determine average channel, bed, and bar widths for 342 channel cells (each 0.5 km long) (Fig. 9). The active channel width of the Big River averages 48.5 m with a coefficient of variation (CV%) of 25% from R-km 171 to the mouth. Channel width increases greatly to its widest below the confluence of Mineral Fork in segments 6, 7, and 8 from R-km 99 to 35, where width is >61 m (+1 s limit) over 25% of its channel length. On average, bar deposits cover 20.3% of the active channel area in the Big River (Table 1). Bar area tends to decrease downstream. Upstream in the mining area, bars cover 23–33% of the channel area in segments 1–3 with all cells containing bars and up to 16% of the segment length with >50% bar area. However, in segments 8–10 along the lower 52 km of the river, bar features only cover 9–16% of the channel area, about a quarter of the channel length contains no bars, and only 0–6% of the segment length contains >50% bar area (Table 1).

The depth of stored sediment in bed and bar deposits was determined using high resolution field surveys of channel morphology and probe depth measurements completed at the 10 storage assessment reaches (Table 2). Storage depth includes the entire thickness of material above the probe refusal elevation and is assumed to be contaminated throughout. Probe depths in bed and bar deposits ranged from 0 to >2 m within a reach, with the single highest probe depth (3.5 m) measured in bed deposits behind the dam at storage site 9. This range of probe depths within a reach is expected as multiple (>30) bar and channel depths were collected and a variety of fluviol
forms and bar types were usually sampled within a sample reach (Table 2). However, mean depth errors at sites were relatively low, and no significant downstream trend was observed among sites (Table 2; Fig. 10). Therefore, single values for average bed depth and bar depth were used for storage calculations at all 500-m channel cell areas below Leadwood. Average bed sediment depth was 0.66 m with a Cv% of 24.5%. Average bar depth was 1.05 m with a Cv% of 13.8%. Sites 9 and 10 were omitted from the analysis for the following reasons. Storage site 9 was located behind an old, but intact, run-of-river mill dam. Therefore, compared to the majority of river length, this reach was not representative as bed sediment storage was enhanced (1.2 m deep) with no subaerial bar deposits (i.e., zero bar depth) because of high backwater. Storage site 10 was located within a relatively steep bedrock reach where average depth to bedrock refusal was very shallow (0.14 m) and bar storage depths were similarly low (0.72 m). Field observations suggest that bedrock reach control like that found at site 10 is very rare, and where it is found, its distribution is patchy.

The USGS data using freeze core technology to measure bar sediment thickness and contamination profiles in bar deposits in Big River (Smith, 2013) confirmed our results using probe depth measurements. The USGS sampled five sites with two to three cores each to determine overall bar thickness and depth of Pb contamination in the <2 mm size fraction. Contaminated sediment depths of 2–3 m measured in the freeze cores fall within the range of the deeper probe depths measured for this study (1.2–3.2 m). Further, USGS bar depths are similar at all five sites and do not appear to change systematically downstream as found in the present study (Smith, 2013). In addition to verifying contamination depth assumptions used in the present study, the results of the USGS study also confirmed that metal concentrations measured in shallow bar grab samples (20–30 cm) were representative of the entire thickness of the deposit.

### 4.1.2. Sediment size trends
Downstream variations in sediment size within bed and bar deposits need to be accounted for to apportion mining-metal concentrations in the <2 mm and 2–16 mm size fractions for storage calculations. In this study, bulk sediment <64 mm represents the total or 100% of the sediment mass evaluated for three size fractions: <2, 2–16, and 16–

### Table 2
Depth of bed and bar deposits.

<table>
<thead>
<tr>
<th>Site number</th>
<th>R-km</th>
<th>Drainage area (km²)</th>
<th>Bankfull width (m)</th>
<th>Reach length (m)</th>
<th>Storage probe points</th>
<th>Bar Mean depth (m)</th>
<th>Bar Max. depth (m)</th>
<th>Bed Mean depth (m)</th>
<th>Bed Max. depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>170.7</td>
<td>638</td>
<td>49.7</td>
<td>515</td>
<td>63</td>
<td>1.04</td>
<td>2.1</td>
<td>0.43</td>
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</tr>
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<td>156.4</td>
<td>318</td>
<td>49.4</td>
<td>484</td>
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<td>2</td>
</tr>
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<td>58.4</td>
<td>534</td>
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<td>0.73</td>
<td>3</td>
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<td>8</td>
<td>32.5</td>
<td>2296</td>
<td>58.6</td>
<td>512</td>
<td>33</td>
<td>0.95</td>
<td>1.2</td>
<td>0.7</td>
<td>2.7</td>
</tr>
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<td>9*</td>
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<td>2386</td>
<td>61.9</td>
<td>660</td>
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<td>0</td>
<td>1.2</td>
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<td>2</td>
<td>2499</td>
<td>56.2</td>
<td>771</td>
<td>40</td>
<td>0.72</td>
<td>1.9</td>
<td>0.14</td>
<td>0.8</td>
</tr>
</tbody>
</table>

| Mean:       | 53    | 488                 | 55                 | 1.05             | 2.2                 | 0.67              | 2.1               |
| Median:     | 53    | 514                 | 56                 | 1.08             | 2.2                 | 0.67              | 2.1               |
| Min:        | 41    | 395                 | 33                 | 0.80             | 1.2                 | 0.43              | 1.2               |
| Max:        | 61    | 534                 | 64                 | 1.28             | 3.2                 | 0.89              | 3.0               |
| SD:         | 6.3   | 50.0                | 9.9                | 0.15             | 0.6                 | 0.16              | 0.6               |
| Cv%:        | 12    | 10                  | 18                 | 14               | 28                  | 25                | 28                |

* Not included in depth analysis.
Polynomial equations (third-fifth order) were used to create downstream trends to predict size distributions for the >2 and >16 mm fractions (Fig. 11). For the entire river below R-km 171, the mean and Cv% values for predicted percent >2 mm fraction are 28.7% ± 11% for bed deposits and 47.2% ± 20% for bar deposits. For bed deposits, the percentage of the >2 mm sediment fraction is highest upstream in segments 3 and 4 (33%) and lowest downstream in segments 8, 9, and 10 (24–25%) (Table 3). For bar deposits, the percentage of the >2 mm fraction is highest in segments 4 and 5 (54–55%) and segment 10 (66%) (Table 3). In general, the coarse and very coarse gravel fraction (16–64 mm) composes from 14 to 29% of bed sediment and 1 to 20% of bar sediment (Fig. 11). Increased sand supply from tailings inputs and from erosion of sandstone bedrock is responsible for increases in the >2 mm size fraction in bar deposits between R-km 155 and 99 (Fig. 11). However, erosion of friable sandstone outcrops is the main source for the increase in the >2 mm size fraction to >80% below R-km 25 in bar deposits (Fig. 11). The textural composition of bar deposits tends to fine downstream in comparison to nearby bed deposits (Table 3). The bar/bed ratio for the percent >2 mm is relatively low at 1.2 in segment 1, rises to 1.7 in segments 4 and 5, drops down to 1.4 in segment 7, and then rises to 2.6 at segment 10.

### 4.1.3 Metal concentration trends

An estimate of the premining Pb and Zn concentrations in channel sediments is needed to determine the mining contribution to storage. Background metal concentrations in channel sediment not affected by mining inputs can vary with soil texture, mineralogy, and bedrock type in the watershed, as well as local factors such as spring seepage and proximity to mineralized outcrops. A sample of 11 channel samples collected in 2011 from above Leadwood was used to approximate background levels for Pb and Zn in the Big River. The mean background and upper 95% confidence limit (+2 s) threshold concentrations were 20 and 34 mg kg\(^{-1}\) for Pb and 39 and 71 mg kg\(^{-1}\) for Zn respectively. The +2 s upper threshold value was subtracted from the total metal concentration.
concentration for all channel samples to determine the mining metal contamination. There have been concerns about the toxic risk posed by sediment metal contamination in the Big River (Mosby et al., 2009). Further, Pb concentrations in channel sediments were found to be above toxic limits for most of the length of the river below mining areas (Roberts et al., 2009). The probable effects concentration (PEC) for metals in sediments above which harmful effects are likely to occur in sediment-dwelling organisms is 128 mg kg\(^{-1}\) for metals in sediments above which harmful effects are likely to occur in sediment-dwelling organisms is 128 mg kg\(^{-1}\) for Pb and 459 mg kg\(^{-1}\) for Zn (MacDonald et al., 2000).

Historical mining inputs have exerted a significant influence on metal concentrations and downstream trends in the <2 mm sediment fraction of channel bed and bar sediment. Average metal concentrations at 26 sites were used to predict downstream variations in metal concentrations in the <2 mm fraction (Table 4). Bed and bar sediments were averaged together at a site, and not stratified by deposit type, as the geochemical variability for paired bed and bar samples was generally within 20–40% CV\(\%\) for Pb and for Zn. Distance-concentration curves were constructed by manual manipulation of trend functions and downstream interpolation to predict downstream trends in metal contamination as the uniform application of single linear, exponential, or polynomial regression equations did not produce curves that adequately fit the spatial distribution of sample data (Fig. 12). In general, metal concentrations in channel sediments tend to remain elevated in mining-affected segments, decrease downstream from mining sources, and drop rapidly below larger tributaries that dilute contaminant concentrations with sediment from nonmining or background sources (Graf, 1996; Ciszewski and Matys Grygar, 2016).

Predicted Pb concentrations in channel sediments exceed the PEC threshold of 128 mg kg\(^{-1}\) for the entire length of the Big River (Fig. 12a). Lead concentrations rose rapidly from <30 mg kg\(^{-1}\) above Eaton Branch at Leadwood to 2105 mg kg\(^{-1}\) at Desloge (Newfields, 2006; USFWS and MDNR, 2007). Lead concentrations remained >1400 mg kg\(^{-1}\) from below Flat River Creek to R-km 140, peaking at 1672 mg kg\(^{-1}\) at R-km 151. Below R-km 140, Pb concentrations decreased exponentially to about 300 mg kg\(^{-1}\) below the confluence of Mineral Fork at R-km 99. Dilution by background sediment from Belews Creek at R-km 34.5 reduced Pb concentrations to about 130 mg kg\(^{-1}\) in lower channel segments with a slight increase near the mouth. High Pb concentrations below the confluence of Flat River Creek (R-km 155) are not surprising given that the three mines in that tributary watershed produced 65% of the tailings and 57% of the Pb during the mining period. Interestingly, Pb concentrations decrease below Turkey Creek at R-km 136.1 even though it drained the longest operating mine in the Old Lead Belt at Bonne Terre. Highly contaminated sediment is available in Turkey Creek as demonstrated by four channel sediment samples collected in 2011 that contained 3000–5000 mg kg\(^{-1}\) Pb and 500–1000 mg kg\(^{-1}\) Zn. However, the relatively small drainage area of Turkey Creek (9.4 km\(^2\)) probably limits the total supply of contaminated sediment inputs to the Big River (1031 km\(^2\)). At the segment scale, average Pb concentrations were >1100 mg kg\(^{-1}\) in segments 1–3 and peaked at 1554 mg kg\(^{-1}\) in segment 2, decreasing to <200 mg kg\(^{-1}\) in segments 9 and 10 (Table 4).

Predicted Zn concentrations in channel sediments exceed the PEC of 459 mg kg\(^{-1}\) for 49 km of the Big River from Leadwood almost to Mill Creek (Fig. 12b). Recall that Zn concentrations in tailings inputs to the Big River were highest at Leadwood (mean = 4691 mg kg\(^{-1}\)) and moderately high at Desloge (1243 mg kg\(^{-1}\)) (Jackson et al., 1935; Newfields, 2006; USFWS and MDNR, 2007). Reflecting these higher inputs to the Big River above Flat River Creek, Zn concentrations in channel sediments rise rapidly from <60 mg kg\(^{-1}\) above Leadwood

### Table 3
Contaminated sediment storage in channel sediment (<64 mm bulk fraction).

<table>
<thead>
<tr>
<th>Segment number</th>
<th>R-km</th>
<th>Bulk volume (m(^3))</th>
<th>&lt;2 mm Bed (%)</th>
<th>Bulk mass Mg Segment (%)</th>
<th>&lt;2 mm Bed (%)</th>
<th>Dolomite (%)</th>
<th>Other (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>171</td>
<td>540,831</td>
<td>30.1</td>
<td>1,136,508</td>
<td>8.7</td>
<td>32.2</td>
<td>13.3</td>
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<tr>
<td>2</td>
<td>155</td>
<td>283,019</td>
<td>32.0</td>
<td>591,741</td>
<td>4.5</td>
<td>35.5</td>
<td>19.9</td>
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<tr>
<td>3</td>
<td>144.5</td>
<td>452,152</td>
<td>32.8</td>
<td>884,488</td>
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<td>39.9</td>
<td>15.8</td>
</tr>
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<td>4</td>
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<td>544,387</td>
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<td>1,131,892</td>
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</table>

Avg. or total: 6,244,036    31.6 a 29.0a 47.0a 13,105,385 100 33.0a 3.3a 63.7a

### Table 4
Channel sediment and metal storage.

| Segment number | R-km | <2 mm (mg kg\(^{-1}\)) | Pb storage Mg Segment % | Dolomite %
<table>
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<tr>
<th></th>
<th></th>
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</thead>
<tbody>
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<tr>
<td>1</td>
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<td>152</td>
<td>83</td>
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</table>

Avg. or total: 618 502 4042 52.7 1818 14.4

\(^{a}\) As described in the text, assumes dolomite fragments contain 4415 mg kg\(^{-1}\) Pb and 1366 mg kg\(^{-1}\) for segment 1 and 307 mg kg\(^{-1}\) downstream of Flat River Creek.
and peak at 2985 mg kg\(^{-1}\) at R-km 163.4 near the Desloge mine (Fig. 12b). From that point, Zn concentrations drop rapidly to 800 mg kg\(^{-1}\) at Flat River Creek and then remain elevated at that level until R-km 140. Below R-km 140, Zn concentrations decrease gradually below Terre Bleue Creek (R-km 144.5) and Mill Creek (R-km 115.5) to 300 mg kg\(^{-1}\) and remain <200 mg kg\(^{-1}\) from R-km 101 to the mouth. By segment, Zn concentrations are highest in segment 1 and then generally decrease in a negative exponential trend all the way to the mouth (Fig. 12b; Table 4).

4.1.4. Dolomite fragment trends (2–16 mm fraction)

We used dolomite fragments sampled from bar deposits as tracers to indicate the movement of chat-sized tailings (Figs. 6 and 12). Bulk percentages are 3% at Leadwood (R-km 170) and rise to >20% from R-km 156 to 137, with a peak of 26% at R-km 145. From R-km 137, fragment contributions drop sharply to 5% at R-km 130, then gradually decrease to <1% at R-km 121, and are typically absent in bar deposits below Mill Creek at R-km 116.5 (Fig. 12). At the segment scale, dolomite fragments are only found in significant abundance in segments 1 (13%), 2 (20%), and 3 (16%) (Table 3). This distribution indicates that chat tailings in the 2–16 mm size range have been transported a maximum distance of about 30 km over a period of 120 years, averaging about 250 m annually.

4.1.5. Contaminated sediment storage

To determine the metal content of the chat tailings fragments, samples of 4–8 mm particles were selected from seven sites, powdered in a ball mill, and subjected to XRF analysis for Pb and Zn. The average concentration of Pb was 4415 mg kg\(^{-1}\) with no significant difference between samples collected above and below Flat River Creek. In comparison, at the Federal Mill, which produced more than half of the Pb in the watershed, chat wastes typically contained 3000–5000 mg kg\(^{-1}\) Pb (Jackson et al., 1935). However, Zn concentrations in three samples from segment 1 below Leadwood averaged 1366 mg kg\(^{-1}\), while the four samples collected below Flat River Creek contained much lower concentrations and averaged only 307 mg kg\(^{-1}\) Zn. These differences reflect the higher concentration of Zn in the Leadwood and Desloge tailings released to segment 1 in contrast to lower Zn tailings entering the Big River from Flat River Creek. The average concentrations were applied to the mass of dolomite fragments stored in channel sediments to estimate metal storage. For Zn, the higher value was used for segment 1 and the lower value applied to segments 2, 3, and 4.

Fig. 12. Downstream trends in metal concentrations in channel sediments (<2 mm) and the abundance of dolomite fragments (2–16 mm) in bar samples. Segments are indicated by the numbers at the top of the plot. Note that PEC values are 128 μg kg\(^{-1}\) Pb and 459 128 μg kg\(^{-1}\) Zn (MacDonald et al., 2000).
(2–16 mm), and 63.7% uncontaminated gravel (i.e., nondolomitic gravel; 2–64 mm). About 20% of contaminated channel sediment is stored in the three mining segments (1–3) and 40% in St. Francois County above R-km 99. Overall, fine sediment (<2 mm) provides 29% of the contaminated sediment storage in bed deposits and 47% in bar deposits. While dolomite fragments contribute relatively little mass (3.3%) to the river as a whole, they account for 13–20% of channel sediment storage in the mining segments.

### 4.1.6. Metal storage trends

Channel bed and bar deposits below Leadwood store 4042 Mg of Pb and 1818 Mg of Zn from historical mining sources (Table 4). The three mining segments account for 72.4% of the Pb and 77.3% of the Zn stored, even though these segments comprise only 22% of the total channel length evaluated. Metal storage is much lower farther downstream below Mineral Fork in Jefferson County where segments 6–10 account for 58% of the contaminated river length but store only 14.1% of the Pb and 8.9% of the Zn. Although dolomite fragments were generally limited to the mining area, they account for slightly >60% of the Pb stored in the three mining segments and 47% of the Pb stored in channel deposits overall. In contrast, dolomite fragments account for only 15–23% of Zn in the mining segments and 16.1% overall. The potential importance of the long-term release of Pb and other metals from tailings particles to the river by physical and chemical weathering has not been previously recognized.

### 4.2. Floodplain storage

#### 4.2.1. Floodplain sediment volume

Based on SSURGO soil data, floodplains cover 37.3 km² of area along the Big River from Leadwood to its confluence with the Meramec River (Table 5). Because of increases in valley width, segment floodplain area generally increases by 2–3 times from the mining area (R-km 171–133) to below Mineral Fork (R-km 99). As floodplains become wider downstream, geomorphic complexity increases as the number of different soil-landform features increases from one to four. Floodplain width increases measurably downstream in a fluctuating pattern, reflecting bedrock control and tributary confluence location (Fig. 13).

Floodplains are contaminated above the background threshold value along the entire length of the Big River below Leadwood to depths usually >2 m (Fig. 13). In general, Pb profiles in cores exhibited relatively consistent trends where concentrations rise from background levels, peak in the lower to middle portion of the contaminated zone at 2000–10,000 mg kg⁻¹, and then decrease to 1000–2000 mg kg⁻¹ at the surface (Fig. 14). Zinc profiles are not as consistent or contaminated, but generally show similar trends. This observation is expected because the primary Zn input was far upstream at the Leadwood mine and the supply of Zn to the channel was much less than for Pb. Average contaminated depths for 19 floodplain sites ranged from 2.3–3.1 m and averaged 2.7 m (Fig. 13). In comparison, total bank heights above the thalweg at the same sites ranged from 4.5 to 5.5 m and averaged 5.0 m, about two times the contaminated depth.

Contaminated depths average about 3 m in segments 2–7 before decreasing to 2–2.5 m in segments 8–10. Three factors may have contributed to this pattern. First, bed aggradation caused by historical gravel inputs may have filled in and choked the channel by decreasing channel cross-sectional area, thereby increasing the frequency of overbank floods and sediment delivery to the floodplain (Jacobson, 1995). Second, floodplain width (controlled by variations in valley geology) may have influenced overbank deposition rates. For a given drainage area, the depth of overbank deposition can be lower for wide (sediment deposition is spread out across a larger area) and for narrow valleys (higher flow velocity and transport capacity) but is higher in intermediate wide valleys (Magilligan, 1985). Finally, additional sediment supply from mining sources or local tributaries may have increased floodplain sedimentation rates at the segments above Mineral Fork.

### Table 5

**Floodplain sediment and metal storage.**

<table>
<thead>
<tr>
<th>Segment number</th>
<th>R-km</th>
<th>Floodplain area (m²)</th>
<th>Floodplain width (m)</th>
<th>Soil-landform Distribution (%)</th>
<th>Contaminated sediment storage</th>
<th>Pb storage</th>
<th>Zn storage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td>21.9</td>
<td>1465</td>
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</tbody>
</table>
4.2.2. Floodplain concentration trends

Sediment samples from the lower portions of cores or bank exposures extending into premining deposits were analyzed for metals to determine natural background concentrations. Twenty-three cores were evaluated, including two from above Leadwood, nine within the three mining segments, and four more from above Mineral Fork (R-km 99). The average background metal concentration and 95% upper confidence limit (+2 s) threshold was 23 and 71 mg kg\(^{-1}\) for Pb and 75 and 169 mg kg\(^{-1}\) for Zn respectively. Toxicity thresholds have been estimated for Big River floodplain soils based on ecological harm to native plants at 451 mg kg\(^{-1}\) Zn (Stroh et al., 2015) and songbirds at 345 mg kg\(^{-1}\) Pb (Stratus Consulting, 2014). Average Zn concentrations in contaminated floodplain deposits exceed 451 mg kg\(^{-1}\) from Leadwood to Mill Creek (R-km 115.5). Lead concentrations exceed 345 mg kg\(^{-1}\) in all floodplains sampled below Leadwood.

Average concentrations of metals in the contaminated portion of overbank deposits at 19 sites were used to quantify downstream trends (Fig. 15). A polynomial curve was used to describe the downstream trend in Pb concentrations. The two high Pb values above 3000 mg kg\(^{-1}\) at R-km 132.8 and 118 include sites with only one core available for analysis and only three samples for each, therefore more weight was put on the trend line to follow other sites with values based on the average of three or more vertical profiles. Lead concentrations \(>2000\) mg kg\(^{-1}\) in floodplains extend 40–50 km downstream from the mining area, suggesting high mobility and a supply of fine tailings particles during mining and, to some degree, post-mining periods. Average floodplain Pb concentrations then level off below R-km 80 to about 1000 mg kg\(^{-1}\) where they remain until reaching the mouth where they increase somewhat to 1500 mg kg\(^{-1}\). This increase in Pb contamination is reproducible and we believe it may indicate the deposition of suspended sediment carrying fine tailings or slimes during backwater conditions when the Meramec River was in flood.

At the segment scale, Pb concentrations are highest (\(>2000\) mg kg\(^{-1}\)) in segments 2–4 in St. Francois County and then drop below 1000 mg kg\(^{-1}\) in segments 7–9 (Table 5).

Downstream trends in average Zn concentrations in contaminated floodplain deposits could not be adequately defined by a specific equation. Therefore, manual fitting was again used to predict concentration values to calculate metal storage (Fig. 15b). Peak Zn concentrations \(>2000\) mg kg\(^{-1}\) occur at R-km 158.1 and 156.1 in several floodplain cores below Leadwood (but above Flat River Creek near Desloge), again underscoring the Leadwood mine source for significant Zn pollution. Sampling density is relatively high below the Desloge Mine, with peak Zn concentrations detected in five cores with a total of 28 samples. Below Flat River Creek, average floodplain concentrations drop sharply downstream to 500 mg kg\(^{-1}\) Zn near Mill Creek and then gradually level off to about 180 mg kg\(^{-1}\) Zn below Mineral Fork and all the way to the mouth. At the segment scale, Zn concentrations are highest in segments 1 (1347 mg kg\(^{-1}\)) and 2 (1666 mg kg\(^{-1}\)) and then decrease to \(<200\) mg kg\(^{-1}\) below Mineral Fork at R-km 99 (Table 5).

4.2.3. Contaminated sediment and metal storage in floodplains

The floodplain deposits sampled for this study averaged 96% fine sediment (\(<2\) mm) based on the results of grain-size analyses performed on 181 floodplain samples representing 33 different cores from 17 sites.
Nineteen percent of the floodplain samples contained very fine and fine gravel (2–8 mm), which fall within the expected ranges for floodplains in soil survey reports (i.e., Sturkie <15%; Haymond <10%; Wilbur 0%; and Kaintuck <25%) (Brown, 1981; Skaer, 2000; Skaer and Cook, 2005). Because dolomite fragments were rarely found in floodplain deposits, we assumed that 96% of the total storage mass of contaminated floodplain material was <2 mm in size and contaminated, while the coarser fraction representing 4% of the mass was considered uncontaminated by mining sources.

Overall, ~96 million m$^3$ (144 million Mg) of contaminated floodplain deposits are stored along the Big River (Table 5). Given the relatively narrow width of floodplain areas and shallow contaminated depths in the upper segments below Leadwood, only about 16% of the contaminated sediment storage is within the mining area (34% in St. Francois County above R-km 99). Contaminated sediment has been transferred downstream to floodplains in Jefferson County where about one-third of the storage is located within the three most downstream segments. In total, 184,507 Mg of Pb and 34,299 Mg of Zn are stored in floodplain deposits (Table 5). Lead storage is uniformly distributed downstream with 72.1% stored in the three mining segments and 94% in St. Francois County.

5. Discussion

5.1. Amount and distribution of mining sediment and metal storage

Mining in St. Francois County released 264 million Mg of tailings containing 508,000 Mg of Pb and 386,000 Mg of Zn to the Big River watershed between 1864 and 1972. Overall, only 22% of the total mass still remains at mining sites within stabilized chat piles and tailings ponds ranging from 19% for the Flat River subdistrict (Elvins, Federal, and National mines) to 28% on-site at Leadwood and Desloge (Newfields, 2006; USFWS and MDNR, 2007). While large volumes of tailings were removed from mining sites for construction and agricultural purposes (Wright, 1918; Mosby et al., 2009), we estimate that about 37% of the Pb (188,549 Mg) and 9% of the Zn (36,117 Mg) originally discharged in tailings wastes is presently stored in channel and floodplain deposits along the Big River (Tables 4 and 5). Overall, ~96 million m$^3$ of contaminated sediments stored in floodplain deposits, which represents 93.9% of the total (i.e., channel + floodplain)
storage. By mass, floodplains store ~144 million Mg of contaminated sediment, which is 91.6% of the total storage (Table 5). About 6.2 million m$^3$ (only 6.1% of the total) or about 13 million Mg (only 8.4% of the total) of contaminated sediment is stored within the channel in bed and bar deposits.

The spatial distribution of historical mine and tailings dump sites in the watershed largely explains the present-day contamination trends in the Big River as sediment concentrations of Pb and Zn tend to be highest below mine sites and then decrease in an exponential trend with distance downstream (Pavlowsky et al., 2010) (Figs. 12 and 8). However, storage trends are generally determined as the product of metal concentration and volume (or mass) of the deposit and, therefore, are additionally linked to valley width, channel and floodplain morphology, and fluvial sorting of the different types of mining wastes. Tailings materials primarily entered the main channel at the Flat River Creek confluence (R-km 155) or farther upstream along the Big River (up to R-km 171) (Table 6A). The Leadwood (R-km 171) and Desloge (R-km 160 km) mines in segment 1 discharged 26% of the tailings Pb and 50% of the Zn. However, the highest amounts of contaminated sediment storage are located in downstream segments below R-km 155 (Table 6B). For example, 66% of the contaminated sediment and 49% of the Pb from historical mining is stored along the lower portion of the Big River below R-km 99 - 40 km downstream from Bonnie Terre (the most downstream mine), which was only affected locally by scattered surface mining activities. However, while 94% of Zn is stored above R-km 99 near the mining area as its main input was at R-km 171, only 18% is stored in segment 1 because of downstream transport. While Flat River Creek drained the largest tailings areas of the Old Lead Belt, storage assessments of channel deposits by Hill (2016) and floodplain deposits by the present authors indicate that alluvial储存s in Flat River Creek are relatively small (<3%) compared to the Big River (Table 6). Factors accounting for low storage estimates for Flat River Creek include limited depositional areas due to narrow channels, confined floodplains, and relatively high transport capacity due to higher slope and frequent bedrock outcrops along the channel bed.

Downstream storage patterns are not uniform among coarse channel, fine channel, and floodplain deposits because of variable source input locations, geochemistry and size of tailings particles, and geomorphic storage capacity (Wall et al., 2003; Ciszewski and Matys Grygar, 2016). Geomorphic storage capacity refers to the ability of the floodplain or channel to store sediment for relatively long periods, and it increases with the size of the sedimentation area and the rate of sediment delivery or deposition within it. More than 60% of contaminated sediment storage occurs in downstream segments 6–10 for channel and floodplain deposits (Table 6C and D). The geomorphic storage capacity of the channel system increases downstream because of increases in channel width of up to 50% below Mineral Fork (Fig. 9). Similarly, floodplain storage capacity increases downstream from Mineral Fork because valleys and floodplains are 2–3 times wider than those upstream in the mining area (Table 5; Fig. 13). Overall, the metal concentration in the fine sediment fraction (~2 mm) and the relative abundance of fine sediment in the deposit are the critical variables that exert primary influence on downstream trends in metal concentrations and storage in this study (Figs. 12 and 15). Therefore, increased bar area in the channel and the higher percentage of fine sediment in bar deposits also increase the metal mass per unit channel length (Figs. 2 and 4). Furthermore, the importance of additional metal storage associated with dolomite fragments in channel deposits is another significant factor increasing storage in Big River near the mining area (Table 3; Fig. 11).

For floodplain storage, in addition to valley width, the depth of contaminated floodplain deposits above the background threshold value is also an important factor in explaining spatial variations. Contaminated sediment depths on floodplains are 0.5–1 m thick along the Big River from Flat River Creek to Mineral Fork (segments 2–5) (Fig. 13). This trend may be explained by the control of valley width on floodplain deposition (Magilligan, 1985) or by higher rates of sedimentation associated with historical sediment waves caused by land use changes during the settlement period (Jacobson, 1995; James, 2013). While it is tempting to suggest that the additional tailings inputs from historical mining operations may have increased floodplain deposition rates by higher sediment loads, estimates of tailings contributions to fine sediment storage based on carbonate percentages are only about 5% by mass for contaminated floodplain deposits and 10% for channel sediment. Moreover, direct counts of tailings chat particles indicate an average bulk percentage of about 10% in the channel ranging from 0% in segment 5 to 20% in segment 2 (Table 3). More study is needed to explain the observed variations in the thickness of contaminated floodplain deposits along the Big River.

The storage rate in units of contaminated sediment volume per kilometer of channel length can be used to remove the influence of variable segment length on storage trends to evaluate storage capacity rates for the Big River (Fig. 16). Among the 10 segments, channel storage rates average 35,563 m$^3$ km$^{-1}$ with a Cv% of 16% ranging from 26,954 in segment 2 to 46,536 m$^3$ km$^{-1}$ in segment 7. Storage rates vary downstream with relatively low rates in the mining-affected segments associated with relatively narrow active channel widths. However, channel storage rates increase below Mineral Fork from R-km 99 to 35 where valley width and sinuosity increase dramatically (Skaer, 2000). Below R-km 35, the channel storage rate decreases to similar levels as in the upstream mining areas as bar storage decreases (Table 1). In relative terms, floodplain storage rates are twice as variable as channel rates with an average rate of 550,777 m$^3$ km$^{-1}$ and Cv% of 32% ranging from 212,949 in segment 1 to 852,531 m$^3$ km$^{-1}$ in segment 9. Overall, a significant positive relationship exists between floodplain width and floodplain storage rates ($n = 10, R^2 = 0.879$). In addition, unit storage rates for contaminated sediment in floodplains are about 15 times greater than those for the channel (Fig. 16).

### 5.2. Influence of selective transport on mining sediment storage

The spatial distribution of sediment and metal storage within the Big River appears to be controlled by the selective transport of finer materials farther downstream with the locus of storage shifting farther downstream in the order: coarse channel sediment (chat); fine channel sediment (~2 mm); and floodplain sediment (~2 mm) (Fig. 17). Grain-size characteristics of these three sedimentary components appear to correlate with the downstream extent and distance of peak storage in the Big River. First, mining chat in the coarse (fine gravel) channel component is the least easily entrained for transport, so storage locations are concentrated in upper segments near tailings source areas. While chat wastes were generated early in the mining period

---

**Table 6**

<table>
<thead>
<tr>
<th>Percent of total storage</th>
<th>Percent of total storage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sediment</td>
</tr>
<tr>
<td>Segment</td>
<td>A) Tailings discharged$^d$</td>
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<tr>
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<td>39.4</td>
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<tr>
<td>6–10$^c$</td>
<td>63.2</td>
</tr>
</tbody>
</table>

$^a$ Based on production records in Bureau of Mining Reports.  
$^b$ Flat River Creek watershed, flows into the Big River at R-km 155.  
$^c$ Flat River Creek storage in addition to the Big River totals after Hill (2016) and estimates by authors based on unpublished studies.  
$^d$ Segments 6 to 10 are in Jefferson County Below R-km 99.
Fig. 16. Downstream trends in the contaminated storage rate. Segments are indicated by the numbers at the top of the plot.

As the third sedimentary component, floodplain deposits are derived from suspended sediment dominated by silt- and clay-sized particles (Brown, 1981; Skaer, 2000) including very fine tailings (slimes) that were capable of being transported downstream even in the fine tailings fraction (Fig. 17b). Total Pb storage by mass in fine channel deposits gradually decreases downstream from 0.3% in segment 1 to 0.1% in segment 5, extending about 40 km farther downstream compared to Pb in the chat fraction (Fig. 17b). Peak Zn storage in fine channel deposits also shifts downstream compared to the chat trend, but only by 10–20 km. The highest concentration of tailings Zn entered the Big River far upstream at Leadwood (R-km 171), so most of the Zn is stored within segment 1 at a much greater rate than either sediment or Pb (Fig. 17b). The fine sediment in the channel is generally composed of sand and silt and thus is more easily transported downstream compared to coarser clay grains.

As the third sedimentary component, floodplain deposits are derived from suspended sediment dominated by silt- and clay-sized particles (Brown, 1981; Skaer, 2000) including very fine tailings (slimes) that were capable of being transported downstream even during low-flow conditions (Buckley, 1909). Therefore, the peak of contaminated sediment in floodplains is shifted even farther downstream to segments 7–9 where 7–15% of total storage occurs (Fig. 17c). In contrast, the location of peak Pb storage in floodplains only extends to segments 5 and 6, shifting 30 km farther downstream than the channel Pb and representing about 15% of the total Pb storage (Fig. 17c). Peak Zn storage shows a dramatic shift from segment 1 where the Zn is found in fine channel sediment, to segment 2 where the Zn resides in floodplain deposits that account for over 30% of the total storage. In addition, the downstream limit of major Zn storage shifts from segment 4 in the channel to segment 6 in the floodplain which contains 4% of total storage (Fig. 17c).

Increased geochemical mobility of Zn may have influenced the downstream concentration and storage trends for Zn. Given the carbonate and sulfide ore mineralogy of tailings in the OLB and neutral to alkaline water/sediment chemistry of the Big River, the solubility and overall environmental mobility of Zn tends to be greater than that for Pb (Smith and Schumacher, 1991, 1993; Miller and Orbock Miller, 2007; Stroh et al., 2015). Therefore, the large shift in relative Zn storage downstream from the mine source in floodplain deposits compared to channel deposits may be the result of the geochemical release of soluble Zn from channel deposits near the mines and binding by fine-grained sediment, iron (Fe) manganese (Mn) oxide coatings, and organic matter in surrounding stream and pore waters downstream (Herrmann et al., 1981; Chapman et al., 1988). Secondary Fe-Mn oxides have previously been identified in contaminated sediments in the Big River (Schmitt and Finger, 1982; Smith and Schumacher, 1991, 1993). They can bind and coprecipitate metals in mining areas as well as release them to the water column during acidic or low oxygen conditions (Horowitz, 1991). Further, groundwater seepage into the channel from underground mine workings can be a source of dissolved Fe and Mn that forms oxide coatings on sediment shortly after entering the channel (Smith and Schumacher, 1993; Newfields, 2006). Once attached to silt- and clay-sized particles, fluvial processes can sort by size, transport downstream, and selectively deposit translocated Zn into overbank floodplain storage (Bradley, 1989; Bradley and Cox, 1990).

6. Conclusions

Widespread watershed disturbances by historical European settlement and large-scale mining activities in the Old Lead Belt coincided in history to produce an episode of contaminated legacy sediment deposition along 171 km of the Big River in the Ozark Highlands of southeastern Missouri. A geomorphic assessment of the Big River was implemented to improve our understanding of this legacy deposit and the magnitude and distribution of contaminated sediment storage in river systems draining the Ozark Highlands. Although this study describes contaminated legacy sediment on floodplains along the Big River below Leadwood, uncontaminated legacy deposits also occur on floodplains upstream of the mining area and along its major tributaries. Channel sediments and floodplain deposits are contaminated with Pb to toxic levels along the entire 171-km length of the Big River below Leadwood. Toxic concentrations of Zn in the channel and floodplain sediments extend about one-third of the distance (50–60 km) to the mouth. Mean concentrations in floodplain cores >2000 mg kg⁻¹ for Pb and >1000 mg kg⁻¹ for Zn extend 40–50 km downstream from the mining area in association with the supply of fine tailings particles that are easily dispersed downstream in the suspended load. Mean concentrations in channel bed and bar sediments ranging from 1400 to 1700 mg kg⁻¹ for Pb extend 30 km below the mines, while Zn concentrations of 1000–3000 mg kg⁻¹ extend 20 km downstream. Coarse tailings have been transported a maximum distance of about 30 km along the 171-km length of the Big River over a period of 120 years. Coarse dolomitic chat fragments in the 2–16 mm channel sediment fraction provide significant storage of Pb.
and Zn in the Big River. While the storage of dolomite fragments is relatively low for the entire river system (3.3%), this component represents 13–20% of the bulk sediment storage mass in the channel and can contain ∼4000 mg kg⁻¹ Pb and >1000 mg kg⁻¹ Zn. Indeed, mining chat accounts for 52% of the Pb and 14% of the Zn stored in channel sediment in the Big River below Leadwood.

Overall, we estimate about 37% of the Pb and 9% of the Zn originally released to the watershed in tailings wastes from concentration mills remains stored in the Big River. Moreover, ∼7 million Mg of tailings were added to the river producing a total of 157 million Mg of contaminated sediment stored in channel and floodplain deposits (63,000 Mg km⁻² of drainage area) with 144 million Mg (92%) located in floodplain deposits typically contaminated to depths of 1.5–3.5 m. The extent of mining contamination in the Big River is significant at the global scale. Some watersheds store more mining wastes such as the 1.5 billion Mg of hydraulic mining sediment in the Bear and American rivers in California (144,000 Mg km⁻²) (James, 1999) and 240 million Mg of tailings in the Kawerong-Jaba River system from the Panguna copper mine on Bougainville Island, Papua New Guinea (685,700 Mg km⁻²) (Archer et al., 1988; Jeffery et al., 1988). A recent review of major tailings dam failures reported a range of releases from 340,000 Mg to 13 million Mg (Kossoff et al., 2014). However, Big River mining sediment storage exceeds some notable mining districts in the USA. Only about 42 million Mg of tailings from the Homestake gold mine were stored in floodplains along the Whitewood Creek-Belle Fourche River system in South Dakota (2320 Mg km⁻²) (Marron, 1992). Further, 11 million Mg tailings from gold mining along Silver Bow Creek and copper mining at Butte were stored in floodplains and wetlands along the Clarks Fork River in Montana (471 Mg km⁻²) (Moore and Luoma, 1990).

The downstream distribution of contaminated sediment and metal storage is influenced by fluvial sorting and selective transport of finer sediment farther downstream and into overbank floodplain areas. About three-fourths of the contaminated channel sediment is located within 25 km of the mining area, compared to just 16% of the contaminated floodplain sediment. A total of 188,549 Mg of Pb and 34,299 Mg of Zn are stored in channel and floodplain deposits. Channel bed and bar deposits store 4042 Mg of Pb and 1818 Mg of Zn. Most of the metal mass (82% for Pb and 88% for Zn) is stored within 25 km of the mines (i.e., segments 1–4). Coarse dolomite tailings fragments account for about 60% of the Pb stored in channel sediment near the mines. Most of the metal mass in the Big River system is stored in the floodplains that contain 98% of the Pb (184,507 Mg) and 95% of the Zn (34,299 Mg). Only 24% of Pb is stored within 25 km of the mining area in floodplains, while 85% of the Zn is stored close to the mining area.

Environmental assessments of streams in mining areas typically focus on evaluating metal concentrations in the <2 mm or finer fractions because these particles tend to be more geochemically active and available to biota compared to coarser sediment (Horowitz, 1991). Indeed, elevated levels of metals have been found in aquatic plants and fish in contaminated segments of the Big River (Schmitt and Finger, 1982; Gale et al., 2002, 2004). In addition, mussels are less abundant and less diverse in channel locations below mining sites where metal concentrations exceed PEC limits (Roberts et al., 2009).

This study emphasized the geomorphic approach to describing the distribution of mining contamination in channel and floodplain sediments of the Big River (Lecce and Pavlowsky, 2014). An adequate understanding of the rates at which geochemical processes affect the weathering of mining sediment and thereby influence metal solubility and chemical redistribution among temporary and long-term sediment storages is lacking. However, as the weathering of coarse sand tailings and chat progresses over time, the mass of metals in transport or storage may shift to finer sediments in more mobile and biologically available forms. This investigation shows that the distribution of contaminated sediment in the Big River can be explained largely as a function of sediment source and transport phenomenon (Pavlowsky et al., 2010). Coarse mine wastes (chat tailings) presently account for over half of the mining Pb stored in Big River channel sediments. These coarse sediments may be an important source of metals to stream water in the future because of weathering by abrasion and dissolution of contaminated particles in channel sediments. Further, the magnitude and basinwide distribution of Pb and Zn storage in legacy floodplain sediments ensures that remobilization by bank erosion will be a continuing problem for water quality far into the future.

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References


Jacobson, R.B., 1995. Spatial controls on patterns of land-use induced stream disturbance at the drainage-scale—an example from gravel-bed streams of the Ozark Plateaus, Missouri. Natural and Anthropogenic Influences in Fluvial Geomorphology, Geophysical Monograph 89. American Geophysical Union.


