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Downstream Dispersal of Fine Tailings, Chat and Metals in Channel Sediment of Big River, Old Lead Belt, Southeast Missouri

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DOWNSTREAM DISPERSAL OF FINE TAILINGS, CHAT AND METALS IN CHANNEL SEDIMENT OF BIG RIVER, OLD LEAD BELT, SOUTHEAST MISSOURI

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Master of Science, Geography and Geology

By

Jennifer Pace Witt

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DOWNSTREAM DISPERSAL OF FINE TAILINGS, CHAT AND METALS IN CHANNEL SEDIMENT OF BIG RIVER, OLD LEAD BELT, SOUTHEAST MISSOURI

Geography, Geology, and Planning

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ABSTRACT

In St. François County, Missouri, compromised above-ground tailings piles and containment ponds from historical mining activities in the Old Lead Belt released considerable amounts of dolomitic, Pb- and Zn-contaminated waste sediments to the Big River, contributing to significant downstream floodplain and channel sediment contamination. Previous studies have documented the effects of heavy metals on Big River biota and water quality, as well as benthic habitat disruption resulting from the influx of small sediments. Few have considered the effects and future contamination risk of the coarse waste sediments (2-16 mm in diameter), locally called "chat", which retain high Pb and Zn concentrations and can constitute over 40% of the <32 mm fraction in channel bar deposits below mining sources. This study examined Big River channel bar sediments between Leadwood and Washington State Park and sought to 1) quantify the percentage of dolomite tailings in downstream channel bar deposits, 2) determine the downstream extent of chat transport from mine waste input sources, 3) evaluate the fine sediment Ca, Pb, and Zn concentrations and their relationship to mine waste, and 4) evaluate the future contamination potential of coarse chat in bar deposits in the Big River. The study showed an overall increase in the average percentage of 2-16 mm sized sediments within bar deposits below mine locations which decreased with distance downstream. Within the study area, dolomite tailings percentages in bar sediments <32 mm peaked near Flat River Creek with close to 80% in 2-4 mm, 65% in 4-8 mm and 20% in 8-16 mm size fractions. The percentage of dolomite dropped to 5% for 2-16mm sediments around 40 km below Flat River Creek while the <2 mm dolomite percentages remained near 10% as far as Washington State Park (50 km downstream from Flat River). Heavy metal concentrations peaked just above Flat River with <2 mm sediment Pb levels as high as 8,700 mg/kg and almost 12,000 mg/kg for Zn. Pb and Zn concentrations decreased with distance downstream but remained above PEC toxic levels throughout the study area. Transport rates between 350 m/yr for 2-4 mm and 175 m/yr for 8-16 mm sediments indicate high residence times within the channel for these sediments. Further, coarse tailings contain high Pb concentrations which may be released to the aquatic environment by geochemical weathering and abrasion due to reworking and transport during flood events.

KEYWORDS: Mine waste; Pb and Zn contamination; chat; coarse tailings; channel bar deposits; Big River, MO; Old Lead Belt, MO

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I dedicate this thesis to Karen – once lost and now found, and

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INTRODUCTION

Since the late 1800s, the advancement of human industrialization has prompted rapid environmental changes and disturbances. Significant environmental consequences are seen in the persistent effects of 19th and 20th century lead (Pb) and zinc (Zn) sulfide mining practices on river and stream systems across the United States (Miller and Orbock-Miller, 2007). Rapid settlement and land use changes in mining areas increased runoff and flooding, disturbed riparian corridors, and affected fluvial sediment supply (Jacobson and Primm, 1997; Owen et al., 2011). Base-metal ore mining and milling processes generated large amounts of small (<16 mm diameter) waste sediments which retained high amounts of Pb and Zn and were typically stored close to main river systems in above-ground waste piles or as fine slurries in containment ponds (Pavlowsky et al., 2010; United States Environmental Protection Agency (USEPA), 1981). Poor management of these tailings sites frequently resulted in substantial sediment releases to river systems and the environment. The resulting heavy metal contamination and geomorphic alterations to streams and riparian habitats have increased riverine vulnerability worldwide and, in many cases, fluvial recovery times have been significantly lengthened or even permanently disrupted (Graf, 1977; Meneau, 1997; Miller and Orbock-Miller, 2007, Ciszewski and Grygor, 2016, Hudson et al., 1999). In fact, Miller and Orbock-Miller (2007) reported that contamination due to historical mining activities represents one of the costliest remediation projects in the U.S.

An influx of mine wastes in streams can disrupt stream flow, alter water chemistry, reduce water quality, prompt geomorphic changes, disrupt riparian and benthic habitats, and release toxic heavy metals into the water and surrounding environment (Bradley, 1989; Coulthard and Macklin, 2003; Graf, 1979; Miller, 1997). While dissolved metal ions pose the highest risk to humans and the environment, close to 90% of contaminants in river systems are

associated with, and transported in, solid phase by some sediment form (Salomons and Forstner, 1984; Coulthard and Macklin, 2003; Miller, 1997). Miller and Orbock-Miller (2007) stated sediments act as a sink for heavy metals and that concentrations in these sediments often exceed that of the dissolved load. Further, Macklin et al., (2006) reported wastes generated by milling and beneficiation processes provide the largest contribution of metal contaminants to fluvial systems. The complex hazards presented by these wastes are strongly influenced by their distribution within the fluvial system, the phase of the residual metals, and the energy and geomorphology of the stream. These factors are unique between river systems and ultimately affect the bioavailability and future release of the contaminant (Miller, 1997; Miller and Orbock-Miller, 2007).

Generation and Storage of Mine Sediments

Historically, once a commercially viable mineral resource was located, the metal-bearing rock was harvested, crushed, and ground into pieces <16 mm in diameter to dissociate the minerals from the host rock (Bussiere, 2007; USEPA, 1981). The terms "mine", "waste", or "gangue" sediments refer to pieces of leftover host rock and ore fragments which were generated and discarded after the Pb and Zn mining, milling, and beneficiation processes. Frequently these sediments are referred to as "tailings" and, in some local areas, the coarser mine wastes (2-16 mm) are called "chat" (Bussiere, 2007; USEPA, 2007). Metals were separated and removed from the gangue sediments through dry, gravimetric and wet, chemical beneficiation processes (Bussiere, 2007; Macklin et al., 2006).

Throughout the 20th century, poor waste management practices allowed the release of large quantities of waste sediments to streams and their surrounding environments (USEPA,

1981; Lewin and Macklin, 1987; Bussiere, 2007). After milling, coarse waste sediments (2-16 mm) were often stored in massive, above-ground waste heaps which were typically uncontained and left open to the elements (Wickland et al., 2010). Weathering, steep slopes, flooding and mass wasting events all contributed to these coarse wastes slumping into rivers (Bussiere, 2007; USEPA, 1981). Tailings and slimes (<2 mm) were pumped as slurries into natural geographic depressions and, beginning in the 1930s, into constructed containment ponds and impoundments (Wickland, et al., 2010). Prior to the 1960s, the stability of tailings impoundments was not a critical concern for mining operations. Impoundments were often created using the mine tailings themselves and were frequently insufficient to contain contaminated water and fine sediments (Bussiere 2007; USEPA, 1981). In some cases, contaminated wastewater, uncontained slurry sediments, and the finest airborne particles were released directly into river systems and the surrounding environment (Bureau of Mines, 1948; Pavlowsky et al., 2008; Jennet and Wixson, 1972; Seeger, 2008; Lewin and Macklin, 1987).

Longitudinal Dispersal of Mine Sediments and Contaminants

As described by Miller (1997), streams adjust to transport the amount of sediment and water received from upstream. These adjustments determine the river's form, distribution, and dispersal rates of sediments along its course. Once within the fluvial system, waste sediments are distributed and stored alongside natural sediments. In Graf's 1996 study of the fluvial transport of metal-contaminated sediments, he described this distribution, suggesting the "…principles of geomorphology explain the fate of the contaminants". In other words, understanding how these sediments are transported and where they might be stored aids in predicting their behavior and the present and future risks they may pose.

The longitudinal dispersal of waste sediments is strongly influenced by size, density, and mineral composition. As stated previously, milled sediments are typically <16 mm in diameter. A large influx of sediments in this size fraction often overwhelms the stream's natural sediment load, prompting active transformation including bed and bar deposition and changes to flow, channel slope and form (Adams, 1944; Graf, 1979; Lewin and Macklin, 1987; Miller, 1997). Fluctuations between stream energy, erosion, transport, and deposition vary with slope and catchment areas along a stream's longitudinal profile, prompting selective transport as coarse sediments are deposited within the channel, closer to point sources. Finer deposits usually travel farther downstream or are carried and deposited outside the channel during flooding events (Graf, 1977; Lewin and Macklin, 1987; Huggett, 2011; Miller, 1997; Miller and Orbock-Miller, 2007). In fact, James (1989) found an average of around 26% of a streams total sediment load can be from remobilization.

Graf (1996) found that metal-laden waste sediments did not travel continuously downstream from point sources but were unevenly distributed due to fluctuations in stream-energy. Due to hydraulic sorting, the abundance of sulfide grains decreased downstream as sediments bearing dense sulfides were often found deposited along with coarser sediments in bed and gravel bar features (Lewin and Macklin, 1987; Miller and Orbock-Miller, 2007). The heavier waste particles were concentrated closer to the point source and moved more slowly downstream than metals attached to suspended sediments by sorption. Observations showed declining downstream metal concentrations in sediments were also affected by dissolution of metals to the water column and by dilution, which occurs due to an influx of natural sediments from tributaries or erosion of channel and floodplain features (Lewin and Macklin, 1987; Graf, 1996).

Distribution of metal-laden sediments can also be affected by chemical form (Hudson-Edwards et.al, 1996). Historical beneficiation processes operated at varying efficiencies and mine wastes typically retained high amounts of Pb and Zn (Pavlowsky et al., 2010; 2017). When introduced to fluvial systems, the dispersal, hazards and long-term effects of these sediments depend on a complex relationship between water chemistry, bacterial activity, chemical speciation, oxygen supply, metal concentrations, surface area and binding mechanisms (Bussiere, 2007; Miller and Orbock-Miller, 2007). These factors are often interdependent and represent unique conditions that ultimately control the bioavailability, which is the ability of a contaminant to be taken up and possibly accumulated by biological organisms, and the future release of the contaminant due to physiochemical changes (John and Leventhal, 1995; Davis, 1993; Noerpoel et al., 2020).

Risks of Heavy Metals in the Fluvial System

Due to their high toxicity to humans and wildlife, the presence of lead (Pb) and zinc (Zn) in the environment has been the focus of many studies. Contaminated dust from waste piles and leached heavy metals from tailings impoundments have been shown to harm living organisms and the surrounding environment (Gulson, 1994; Davis, 1993; Lynch et al., 2014; Gale and Wixson, 1979). These metals can contaminate groundwater, soil, streams, and floodplains. On the microbial level, heavy metals decrease the diversity and biomass of microbial communities in soils, the by-products of which often aid in nutrient absorption in some organisms (Park et al, 2020). In addition to health effects, birds and wildlife are negatively affected as habitats are disrupted and food sources are contaminated (Beyer et al, 2013). In plants, Pb hinders growth and interferes with photosynthesis (Agency for Toxic Substances and Disease Registry

(ASTSDR), 2020; Tchounwou et al., 2012, Hudson et al., 1999), and in aquatic organisms, it reduces survival and production rates and negatively affects growth (Allert, 2009; Besser et al, 2009; Erten-Unal et al., 2015).

Harmful Effects of Lead. According to the USFWS (2008), lead is not biologically useful to any living organism and there is no "safe" blood lead level (PbB) for humans. Lead can accumulate to toxic levels in organs, muscle tissues, bones, and teeth and the US Environmental Protection Agency considers lead a probable human carcinogen (Tchounwou et al., 2012). The primary pathway for human exposure is through ingestion of contaminated food or water or inhalation (Tchounwou et al., 2012; Davis, 1993; ATSDR, 2020). In children, lead poisoning can result in serious neurological and behavioral effects, decreased learning ability and intelligence, and may contribute to accelerated skeletal maturation which can result in adult osteoporosis. In adults, there is an increased risk of miscarriage, premature birth and low birth weights (ATSDR, 2020). Further, Pb has been indicated as an endocrine disrupting chemical and has been linked to obesity and diabetes (Park et al., 2020). To cause health effects, Pb must be dissolved in the acidic environment of the stomach and absorbed by the gut (Davis, 1993). In most adults, Pb absorption is minimal, with over 99% leaving the body within a few weeks. Children, however, absorb more than 50% of lead ingested due to their immature and growing systems, a greater proportion of swallowed lead, and greater accumulation in tissues and organs (USHHS, 2004; MDNR, 2008; Tchounwou et al., 2012).

Harmful Effects of Zinc. While Zn is considered essential for various biochemical and physiological functions, it can be harmful in high concentrations. The Agency for Toxic Substances and Disease Registry (ATSDR) (2005) reported one of the most significant sources of Zn in the environment is mine tailings with highest concentrations typically occurring close to

point sources. Pathways of exposure include ingestion, skin contact, and inhalation. In addition to airborne particles, zinc dissolves in water and small particulates adsorb strongly to soils. Zinc concentrates in plants and aquatic organisms and toxic levels adversely affect photosynthesis, plant growth, and leaf color (ATSDR, 2005; Rout and Das, 2003). Respiratory effects of zinc dust inhalation include "metal fume fever", which exhibits flu-like symptoms, and lung inflammation. If ingested in large amounts, humans can experience acute nausea and vomiting, while chronic effects include anemia, pancreatic damage and cholesterol effects. (ATSDR, 2005).

Relationship Between Bioavailability and Speciation. The chemical speciation of heavy metals affects the release, rate of contamination, and bioavailability of the contaminant (John and Leventhal, 1995; Davis et al., 1993; Salomons and Forstner, 1984). Lead and zinc ores frequently occur as sulfides, where lead occurs as galena (PbS) and zinc occurs as sphalerite (ZnS). Pb may also adsorb to or substitute for Fe or Mn, resulting in Pb-bearing ferromanganese oxides (Davis, 1993). Conditions within stream systems increase the risk of heavy metal release. In pH neutral to alkaline waters, sulfides generally have low solubilities. However, in rivers with high levels of limestone and dolomite, despite the buffering effect of carbonate material, weathering and partitioning between solid and liquid phases occur as waste sediments are exposed to frequent transport, erosion, and reworking (John and Leventhal, 1995; Lara et al., 2011; Miller and Orbock-Miller, 2007). Gravel bars are regularly subjected to episodic wet and dry periods as they are inundated during high-flow and then re-exposed once natural flow is restored. High stream flow and flooding events can scour bed and bar sediments, reactivating and redepositing them in bed, bars, and banks downstream. (John and Leventhal, 1995; Miller and Orbock-Miller, 2007).

Effects of Host Rock Lithology. Waste sediment lithology can play an important role in the release and dispersal of sulfides to the environment. As previously mentioned, carbonate sediments, such as those related to MVT deposits, tend to buffer acidic solutions typically produced by sulfide weathering (Leach et al., 1996). In these high pH and pCO_2 environments, evidence suggests that sulfides will alter to more bioavailable carbonate forms (Haferburg and Kothe, 2012; Hudson-Edwards et al., 1996). Carbonate hosts react with carbonic acid, which naturally forms from carbon dioxide in the atmosphere and soils. This is the primary method of carbonate erosion in non-arid regions, however, in these environments, mechanical processes also play a significant role (Emmanuel and Levenson, 2014). Israeli and Emmanuel (2018) found that, due to a higher density of reactive grain boundaries, fine-grained carbonate sediments were found to weather more rapidly and experienced a higher rate of dissolution than coarser grains. As highly reactive particles (such as calcite cements) dissolve, the lower reactive particles become detached, affecting porosity and permeability and ultimately increasing surface area for more weathering. This detachment makes up around 36% of the total weathering rate for carbonates, and in carbonate sediments with both low and high-reactivity minerals, it was noted that a maximum of 50% of the weathering rate occurred as detached particles (Israeli and Emmanuel, 2018).

Old Lead Belt Mining and Contamination of the Big River

A prime example of contamination from Pb and Zn mining wastes is found near the site of one of the largest galena (PbS) deposits in the world (Hagni et al., 1989). Located almost 100 km southwest of St. Louis, Missouri, the Big River and surrounding watershed form the principal drainage system for the "Old Lead Belt" (OLB), one of the largest historic lead-producing sub-

districts of the Southeast Missouri (SEMO) Mining District (Mosby et al., 2009; MDNR, 2008). In this region, most Pb and Zn sulfides occur as carbonate Mississippi Valley Type (MVT) ore deposits and are characteristically composed of dolomitized limestone hosts, mineralized sulfides, and large amounts of dolomite, calcite and quartz cements (Gregg and Shelton, 2012). Galena (PbS) and sphalerite (ZnS) precipitate as large euhedral crystals, collective concentrations of small crystals in dissolution vugs and bedding planes, and finely disseminated particles throughout the dolomite host. Gangue minerals include large quantities of dolomite, along with pyrite, calcite, chert, and drusy quartz (Gerdemann and Myers, 1972; Gregg and Shelton, 2012; Seeger, 2008). Ore grade in the region ranged from 27,000 to 60,000 mg/kg Pb and localized Zn enrichment in OLB ores caused higher Zn concentrations in some locations, with Leadwood being the highest at around 5,000 mg/kg (Pavlowsky et al., 2010).

Until the mid-1800s, miners in the area harvested surface ore deposits with picks and shovels and much of the ore was transported down the river for processing (Eckberg et al., 1981; Seeger, 2008). Once improved technology opened access to large underground deposits, blasting broke apart large ore deposits and created immense underground caverns supported by thick, undisturbed pillars of host rock. The products were hauled to primary underground crushers, then transferred to on-site, above-ground processing mills where millions of tons of ore were further crushed and ground to mechanically dissociate the mineral grains from the host rock (Bureau of Mines, 1948; Hagni et al, 1989).

Milling produced waste sediments <16 mm in diameter which are further classified by size fractions as follows (Owen et al, 2012; Pavlowsky et al., 2008):

Coarse tailings or “chat” (2-16 mm): Often locally called “chat”, crushed gravel to sand-sized rock fragments were typically screened to about 12.7 mm for gravitational separation

processes (USEPA, 2007; Mosby et al., 2009; Pavlowsky et al, 2010). Heavy metals were segregated from the gangue materials as larger chat grains were passed through gravity jigs and finer fractions were processed by automated shaking tables. After initial separation, some of the larger fragments were often returned to the crushers for finer grinding and reprocessing (Bureau of Mines, 1948; Taggart, 1945).

Tailings (0.07 – 1 mm): Fine, sand- to silt-sized sediments were mixed with water and chemicals to create fine slurries. Flocculation chemicals and techniques increased harvest efficiency as sulfide grains were caused to either float to the surface or sink to the bottom. The fine concentrates were dewatered using vacuums and fine filters and then collected and transported for smelting (Bureau of Mines, 1948; Pavlowsky et al., 2008, 2010).

Slimes (<0.06 mm): Grinding and wet separation processes often generated very-fine, powdered sediments (<0.05 mm). Some of this "rock flour" was impossible to contain and escaped into the air and surrounding water. A significant amount of the larger slime sediments (0.032 to 0.2 mm) was captured, mixed with water and flocculation agents, and whipped into a froth. The fine metal particles rose to the surface in a foam, which was then scraped off and passed through dewatering and vacuum processes (Bureau of Mines, 1948; Pavlowsky et al., 2008; Taggart, 1945).

Distribution of OLB Mine Sediments

From the late 1800s until 1972, close to 250 million tons of chat and tailings were generated and stored in above-ground mounds and containment ponds in the Old Lead Belt sub-district (Newfields, 2007). The waste piles grew to mountainous heights, looming over the small mining towns and becoming solid fixtures in the landscape and local culture (Fig. 1). While the

entire region was littered with uncontained and repurposed mine sediments, six main storage sites held the bulk of the stored chat: Leadwood, Desloge, Elvins/Rivermines, Federal, National, and Bonne Terre (U.S. Environmental Protection Agency (USEPA), 2011; Mosby et al., 2009; USFWS, 2008; Pavlowsky et al., 2008, 2010; Owen et al., 2012) (Fig. 2). Each of the piles were located within a kilometer from the Big River or one of its main tributaries and most covered an area of more than 2.6 km^2 (1 mi^2) (Mosby et al., 2009; Pavlowsky et al., 2010).

Throughout peak production and the years following area mine closures, the storage sites remained unsecured, unstabilized, and open to the public (Schmitt et al., 1987; USFWS, 2008). Tailings dams failed and released water and sediments to the surrounding areas. Residents climbed and played in the huge chat piles. Much of the chat material was repurposed and redistributed throughout the area as industrial aggregate, snow and ice control, railroad and road ballast, agricultural lime agents, fortifications for hastily constructed tailings dams, and even fill for sandbags (Newfields, 2007; USHHS, 2004; Asarco, LLC, 2014; USEPA, 2011; Pavlowsky et al. 2010, 2017; www.rootsweb.com).

Figure 1: Historical images of above-ground tailings or “chat” piles. **Left:** The National chat pile rises above the surrounding landscape - c.1949. **Right:** North County Junior High band marches "in the shadow" of the Bonne Terre chat pile (1993). Images: sites.rootsweb.com

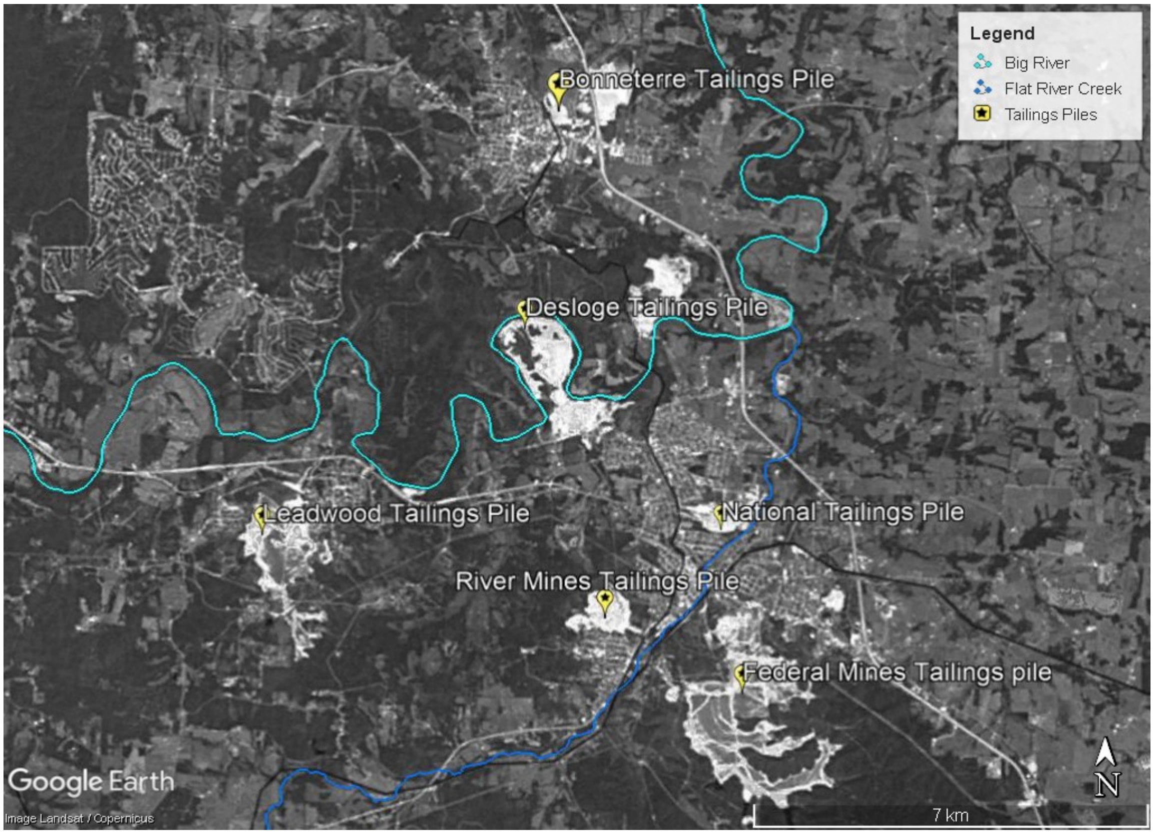


Figure 2: Historical aerial image (1984) of OLB tailings piles. Big and Flat River chat piles appear bright white in this 1984 image, prior to EPA remediation. The six major chat piles include Leadwood, Desloge, River Mines, Federal, National, and Bonne Terre. Image: Google Earth - modified by author

Regular flooding and the high angle of repose in chat piles caused mass wasting events, releasing thousands of chat particles into the nearby Big River and Flat River Creek (MDNR, 2008; Newfields, 2007; Graf, 1977; Jacobson and Primm, 1997; Meneau, 1997). In 1977, one of the largest mass wasting events in the river drew national attention as a large storm caused over 38,000 cubic meters of contaminated mine waste to slump into the river from the Desloge pile (Newfields, 2007; USFWS, 2008). These sediments accumulated as floodplain, overbank, and thick bed and bar deposits. Natural substrates became buried as the new influx of gravel and sand-sized sediments filled the channel and smothered habitats, nesting grounds, and resident benthic organisms in the stream (Besser et al., 2009). As time passed, evidence of environmental

disturbance and heavy metal contamination within the river and throughout the community began to emerge.

Environmental Contamination and Previous Research

Metal recovery during the region's peak production years (early to mid-1900s), averaged from 80-95% efficiency at best. Sediments within the six major chat piles retained an average Pb concentration of 2,000 to 4,000 mg/kg and as high as 10,000 mg/kg for Zn (US Health and Human Services (USHHS), 2004; Newfields, 2007; USFWS, 2008; Pavlowsky et al., 2010, 2017). Background levels in the river, measured upstream from mine sites, ranged between 20-34 mg/kg for Pb and 39-71 mg/kg for Zn (Pavlowsky et al., 2010, 2017). Initially, the sulfides within the chat, particularly Pb, were assumed to be mostly insoluble due to the carbonate nature of the host and the hard water conditions of the region (Jennet and Wixson, 1972; Leach et al., 1996). However, Schmidt et al. (1987) found stream sediments from mine-affected reaches contained fewer residual sulfide metals than expected. Instead, the majority of Pb was found adsorbed to small sediments and in carbonate and oxide-bound forms, suggesting the sulfides in waste particles were continuously becoming more soluble through oxidation processes.

The contamination of the Big River basin and surrounding watershed has been well documented. As early as 1900, claims of dead livestock, poor crop yields and poor fishing were blamed on the thick sludge and slimes being freely dumped into the river and in 1911, legal suits were filed against the lead mining companies in the Old Lead Belt (Faust, 2002). Following the Desloge pile slump, high concentrations of Pb and Zn were reported in the surface water, floodplain, channel sediments and riparian corridor (Allert, 2008; Besser and Rabeni, 1987; Besser et al, 2009; USEPA, 1998, 2011; Newfields, 2007; Owen et al., 2012; Pavlowsky et al.,

2010, 2017). In 1992, as a result of investigations into health and environmental risks associated with the mine wastes by the EPA and Missouri Department of Natural Resources (MDNR), the Big River Mine Tailings Site (BRMT) was placed on the National Priorities List (MDNR, 2008). In 2004, the United States Department of Health and Human Services (USHHS) found at least 17% of the children in the OLB region had elevated blood lead levels (PbB) and several studies correlated high Pb concentrations in surface water and channel sediments to harmful effects in birds and in local aquatic organisms including mussels, fish, clams, and crawfish (Beyer et al., 2013; Gale et al., 2002; Besser, 1987, 2009; MDNR, 2010; Roberts et al., 2009; USFWS, 2008).

In 2007, the Missouri Department of Natural Resources (MDNR) issued a total maximum daily load for the Big River which set toxicity levels for dissolved Pb between 5 to 136 μg/L and Zn at 193 to 211 μg/L. Probable effect concentrations (PEC), which determined sediment Pb and Zn concentration limits for healthy aquatic life, were established at 128 mg/kg for Pb and 459 mg/kg for Zn, based on guidelines developed by MacDonald et al.(2000).

Besser et al. (2009) indicated metal concentrations in pore water and very-fine sediments exceeded PEC thresholds between Leadwood to the confluence with the Meramec River, with the highest levels of Pb contamination between the “Bone Hole”, a low-water bridge site about 5 km downstream from Leadwood, and Hwy E. Further, Pavlowsky et al. (2010) reported an estimated 3.6 million cubic meters of contaminated sediment was stored within the Big River channel (bar and bed deposits) between Leadwood and the Meramec River and around 86.8 million cubic meters was contained in the adjacent floodplains. Preliminary analysis of the in-channel sediments showed varying Pb concentrations by size fraction with around 5,000mg/kg Pb in chat sizes (4-8 mm), 2,500 mg/kg for <2 mm sediments and >10,000mg/kg in slimes (<63μm) (Pavlowsky et al., 2010). Around 85 km of the Big River below mining sites and

around 16 km along Flat River Creek and Shaw Branch were declared impaired and added to the Missouri 303(d) list due to the presence of mine waste and high levels of Pb and Zn (MDNR, 2008). Point sources included near-bank waste piles, drainage from tailings ponds, and confluences with mine-waste affected tributaries. The tailings piles now belong to the Big River Mine Tailings Superfund site declared by the US Environmental Protection Agency (USEPA). Today, all six waste sites have been remediated, capped, and contained. However, there remains an estimated 1.6 Mg of chat and tailings within the channel of the Big River below mine sites and Flat River Creek contains an additional 19,000 Mg (Newfields, 2007; Pavlowsky et al., 2017).

Purpose and Objectives

Most of the sediment studies in the Big River have focused on the distribution of contaminated fine- and very fine-grained sediments (<2 mm) (Pavlowsky et al., 2010; USFWS, 2008). While these small particles tend to be the most mobile for transport and the most available for adsorption of Pb at relatively high concentrations, it is important to remember that voluminous amounts of coarser tailings and chat (between 2 to 16 mm) were released to the Big River during mining operations and storage site failures. These carbonate sediments can contain over 4000 mg/kg Pb and 1000 mg/km Zn, represent 13-20% of the bulk composition of in-channel deposits up to 30 km below mining sources, and remain at risk for weathering, chemical dissolution, reactivation, and reworking (Pavlowsky et.al, 2017). In an expert report provided to the USFWS (2008) for a pre-assessment screen of the Big River Mine Tailings site, Donlan reported that sediment is the most persistent source of metal contamination in the river due to the following: 1) metals tend to adsorb to fine particles (which are abundant in the riverine

environment), 2) sediments move slowly through fluvial systems, and 3) metals take a long time to degrade.

At the time this research was conducted, little was known about the role and specific contributions of coarse tailings (chat) (>2 mm) within the environmental context in the Big River (Pavlowsky et al., 2010, 2017). In 2010, Pavlowsky et al. sampled 25 channel sites between Leadwood and the Meramec and found that in-channel chat sediments can contain residual Pb at concentrations >5,000 mg/kg and constitute >50% of the bulk channel sediment below mining source points in the main stem of the Big River. They detected significant chat presence in bar samples between Leadwood and Bonne Terre which tapered off by Highway E in St. François County. Further, elevated elemental Ca levels (which can indicate dolomite presence) were detected in fine sediments downstream from mining inputs as far as Morse Mill. This preliminary study was neither definitive, nor complete, and further refinement was needed to better understand the effects of chat in gravel bars. More recently, Noerpoel et al.(2020) found released galena was altering to more bioavailable adsorbed species as it moves downstream and, using isotopic analysis, they confirmed the source of the Pb contamination in mine-affected reaches of the Big River is, indeed, the above-ground tailings piles. There are concerns about the environmental risks posed by the physical presence and heavy metal content of the chat in channel bed and bar deposits, as well as the risk of reworking and the downstream migration influence on overall channel stability and aquatic habitats.

The purpose of this study is to increase and refine the understanding of the spatial distribution and ongoing contamination potential of chat-sized (2-16 mm) mine waste sediments deposited in Big River channel bar deposits located downstream from historical mine waste input sites.

Specific research objectives aim to:

1) Establish size and lithology distribution percentages for coarse chat-size fraction (2-16 mm diameter) within Big River in-channel bar deposits below mining input sources.
2) Use chat particles as sediment tracers to evaluate distance, rate of travel, and downstream dispersal of 2-16 mm sediments from point sources.
3) Analyze downstream bar deposits for correlations between dolomite presence and fine sediment (<2 mm) Ca, Pb, and Zn concentrations.
4) Evaluate the potential long-term role of mine waste in the Big River and its significance as a future, ongoing source of Pb contamination.

STUDY AREA

Regional Setting

The Big River is a perennial, gaining, sixth-order stream characterized by incised meanders, shallow riffles, and long pools and located in the eastern portion of the Ozark Plateaus Physiographic Province in Central Missouri (Mugel, 2017; Brown, 1981; Smith and Schumacher, 1991; USDA, 1979). The headwaters begin on Johnson Mountain in Iron County, flow northeast through Council Bluffs Lake, over the dam at the northern outlet of the lake, then north/northeast through Iron and Washington Counties. It flows past the towns of Irondale, Leadwood, Desloge, and Bonne Terre and drains the northern portion of the county (USDA, 1979). The river passes through St François and Washington State Parks, then continues to flow north/northeast through Jefferson County to its confluence with the Meramec River at Eureka, MO, about 40 km southwest of St. Louis (Mosby et al., 2009; Owen et al., 2012) (Fig. 3).

Geology and Soils

The Big River basin is bounded by the sedimentary Salem Plateau and the Precambrian igneous provinces of the St. François Mountains (Gregg, 1985; Smith and Schumacher, 1993; Brown, 1981). In St. François County, the river cuts into the underlying Lamotte Sandstone and Bonneterre dolomite in the Farmington Plain (USDA, 1979). The lithology of the region ranges from the granitic St. François Mountains, through pre-Cambrian rhyolites, to the Mississippian-Meramecian series of the Salem Plateau (Gregg, 1985) (Fig. 4). Upland soils in the area are generally formed in a thin layer of Pleistocene loess overlying cherty dolomite residuum (Pavlowsky et al., 2017).

Figure 3: Map showing Big River and significant locations.

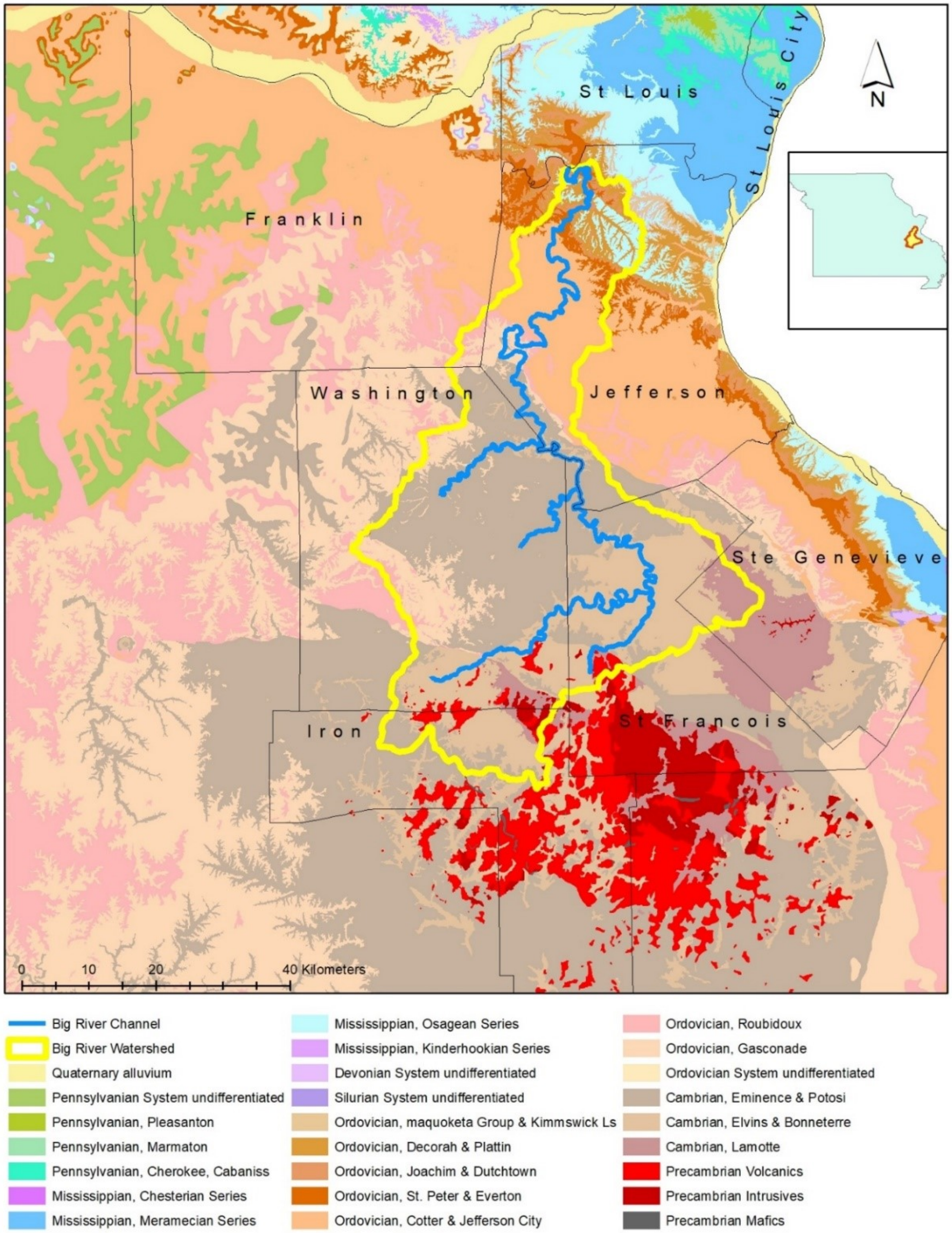


Figure 4: Geologic Map of Missouri. Image by author

The primary sulfide ores of the region include mainly galena (PbS) with lesser amounts of sphalerite (ZnS), pyrite along with its polymorph marcasite (FeS_2), and chalcopyrite ($CuFeS_2$) (Appold and Garven, 2000; Hagni et al., 1989; Seeger, 2008). Cerrusite ($PbCO_3$) was present in surface deposits during early mining operations (Hagni et al. 1989, Seeger, 2008). Gangue minerals include pyrite and marcasite, but the majority are dolomite, calcite, and quartz (Hagni et al., 1989). Most of the mined ore in the Old Lead Belt sub-district was localized near the eastern flank of the St. Francis Mountains in a dolomitized offshore reef complex located in the lower third of the Bonneterre formation, a Cambrian carbonate sequence containing Mississippi Valley-type (MVT) lead-zinc deposits (Gregg, 1985; Gregg and Shelton, 2012). While regionally, most of the Bonneterre is considered limestone, around the St. François mountains the lower Bonneterre consists of a fine-grained dolomite ($CaMg(CO_3)_2$) characterized by digitate stromatolites and calcarentites and it is from this formation that most of the milled chat sediments are derived (Appold and Garven, 2000; Gregg, 1985). It overlies the Lamotte sandstone, a permeable quartz arenite, and is capped by the Davis formation, an impermeable, interbedded limestone, dolomite, and shale formation (Appold and Garven, 2000; Gregg, 1985; Hagni et al. 1989). Other formations present in the region include the Derby-Doerun Dolomite, Potosi Dolomite, Eminence Dolomite, Gasconade Dolomite, and Roubidoux Formation (Fig. 5). Dolomite and calcite cements are commonly found in vugs and pores. It is suggested that dolomitization of the Bonne Terre occurred between the Late Pennsylvanian to Early Permian periods and resulted from warm northward flowing Mg-rich fluids permeating through the lower Lamotte sandstone layer (Appold and Garven, 2000; Gregg, 1985). This was most likely driven by tectonic activity during the Alleghenian orogeny and topographic changes resulting from the uplifted Arkoma basin (Appold and Garven, 2000).

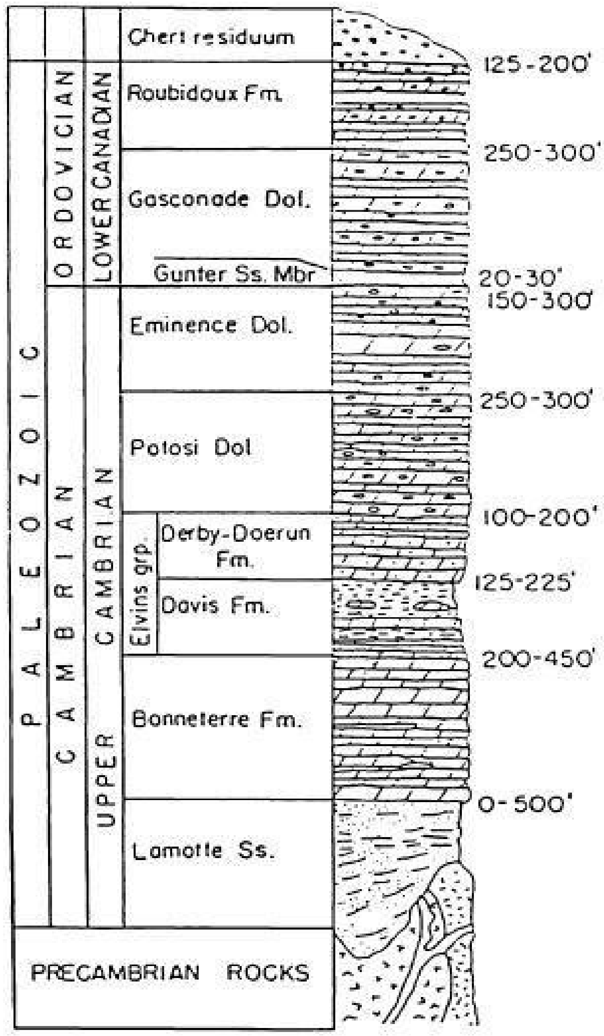


Figure 5: Simplified stratigraphic column, Old Lead Belt, Southeastern Missouri. From Hagni et al., 1989.

Climate and Hydrology

The elevation of St. François County is approximately 279 meters above sea level (masl) and Washington County is around 168 masl. The Koppen classification for this region is Cfa (humid, subtropical) and the annual mean temperature is 13°C. Due to its interior continental location, the region experiences wide temperature changes throughout the year. Winters bring freezing temperatures but are often punctuated with milder temperatures throughout the season.

Summers average 26-32°C, and rarely exceed 37.7°C. Rainfall is abundant, averaging around 127 cm per year, with frequent thunderstorms and occasional extreme events including high-intensity rain, ice storms, and tornadoes. Short drought periods occur nearly every year, but severe drought periods are rare. Low-lying areas commonly experience fog and higher humidity. Daylight hours vary from around 9.5 hours in the winter to around 15 hours in the summer (University of Missouri Climate Center: http://climate.missouri.edu).

The Big River stretches approximately 233 km from head to mouth and ranges in elevation from around 530 m to 130 masl. The steepest gradient is located near the St François Mountains; however, the average gradient is around 1.25 m/km, relatively lower than many other Ozark streams (Meneau, 1997; MDNR, 2008; Owen et al., 2012; Brown, 1981). The Big River watershed is part of the upper Mississippi River basin and drains an area of approximately 2,500 km^2 (Owen et al., 2012; Meneau, 1997; Mosby et al., 2009) (Fig. 6). Within the basin, Meneau (1997) reports over 207 km of permanent streams and eight significant fifth-order tributary streams with overall good riparian and fishing habitats (Table 1). The presence of mine waste has significantly damaged several streams downstream from mining activity. Most of the basin's streams flow through the Salem Plateau and are underlain by Cambrian dolomite, limestone, and shale sequences with outcrops of cherty dolomite and sandstone. The average pH is around 7.2, however, pH has been measured below 7 in August and September, when water levels are lower (Smith and Schumacher, 1991). Average water hardness in the river is 200 mg/L and average alkalinity is 152 mg/L (MDNR, 2010; Meneau, 1997). Groundwater flows generally to the west and is stored in two main aquifers: 1) the shallow Ozark aquifer, comprised of dolomites and sandstones and underlain by granite formations and 2) the deep St. Francis aquifer, composed of Lamotte sandstone (MDNR, 2008).

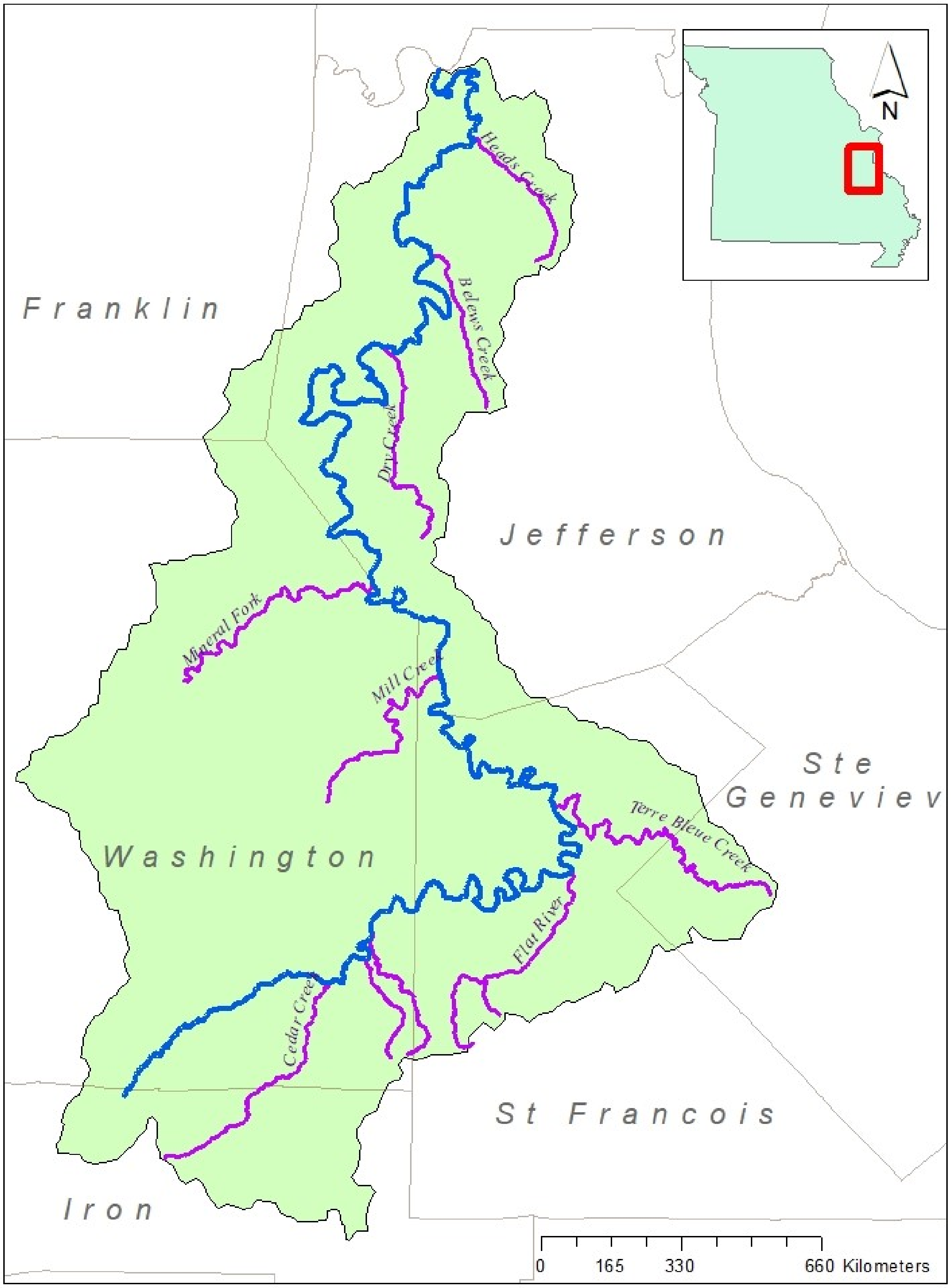


Figure 6: Big River watershed area

Table 1: Tributary streams (5th order) for Big River (After Meneau, 1997)

Stream name	Max order	Watershed Area (km^2)	Length (km)
Belew Creek	5	189.6	11.1
Cedar Creek	5	205	22.7
Dry Creek	5	140	15.4
Flat River	5	137.3	24
Heads Creek	5	134.7	12.4
Mill Creek	5	134	21.4
Mineral Fork	5	489.5	24.8
Terre Bleue	5	173	34.9

There are three active USGS gauging stations located on the Big River: Irondale (07017200), Richwoods (07018100), and Byrnesville (07018500). The Irondale gauge is located upstream of mining activity and reflects background conditions in the river (Smith and Schumacher, 1993). The average annual discharge at Irondale is 5.44 m^3/s (192 ft^3/s). At Byrnesville, the most downstream location, the drainage area is around 917 m^2 and annual discharge is around 25 m^3/s (885 ft^3/s) (https://water.weather.gov). The increase in discharge between Irondale and Byrnesville is likely due to inflow from abandoned mines along the Big River (Newfields, 2007) (Fig. 7). Mean precipitation is typically highest in May (https://water.weather.gov; http://climate.missouri.edu). Flood stage begins at 4.8m (16 ft), with moderate flood stage at 6.1m (20 ft), and major flood stage at 8.5m (28 ft). The highest streamflow on record at Byrnesville occurred in 1993 when waters reached a gauge height of 10.22 m (33.54 ft) and discharge of 1894 m^3/s (66,900 ft^3/s). The most extreme event outside the period of record includes flooding in Aug, 1915 which reached a gauge height of 9.1 m (30.2 ft) and produced an estimated discharge of 2,265 m^3/s (80,000 ft^3/s) (https://water.weather.gov).

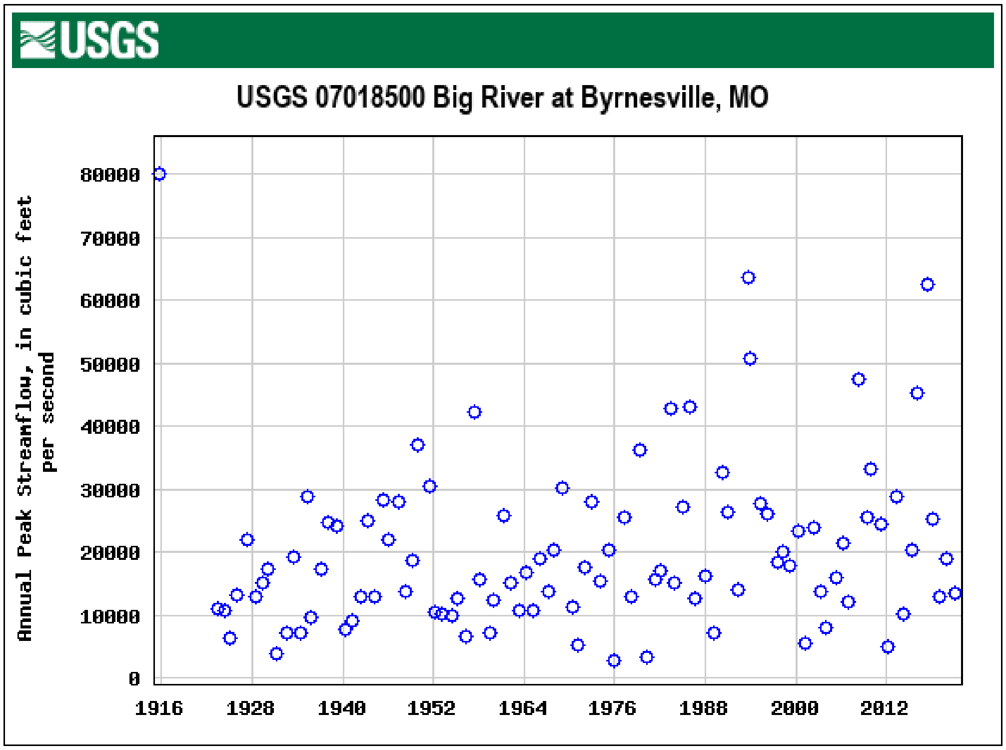


Figure 7: Annual Peak Streamflow, Byrnesville, MO, 1922-2022. Note high water events have been increasing in the last few decades as shown above. Chart obtained from **https://water.weather.gov**

Land use

Prior to significant European settlement, evidence shows geomorphic changes to the rivers and valleys of the Ozark region occurred naturally, prompted by episodic climatic and geologic events. Typical pre-settlement stream deposits in the region included a mixture of gravel and fine, silty sediments (Jacobson and Primm, 1997). Just before the turn of the 19th century, the Louisiana territory, including Missouri, changed from French to Spanish control and American settlers were recruited and encouraged to settle the area (Eckberg et al., 1981). The Louisiana Purchase in 1803 encouraged even more American settlements and by 1820, the American population in Missouri had reached 50,000. By August of 1821, Missouri became the 24th state, admitted as the 12th slave state in the U.S. (Seeger, 2008; Eckberg et al., 1981). By the

late-1800s, large timber operations grew, urban development progressed, and open range burning was used to maintain undergrowth (Jacobson and Primm, 1997; Jacobson and Pugh, 1992). As new settlements concentrated near rivers and waterways, timber and riparian vegetation was cleared, new roads and bridges increased trade, homes and businesses were built, and farmers began planting crops and raising livestock (Eckberg et al., 1981). Rapid land use changes increased runoff and destabilization of riverbanks contributed to increased bank-full and flooding events. Throughout the 1900s, open-range grazing contributed to headward channel migration as riparian corridors were destroyed. Significant channel and valley sedimentation increased as coarse, cherty gravel, no longer secured by vegetation and smaller sediments, was eroded, transported, and deposited downstream (Jacobson and Primm, 1997; Meneau, 1997; Martin and Pavlowsky, 2011).

Presently, most of the SEMO mining district is covered with forestland including deciduous species such as oak, black walnut, and hickory. There are several non-operational underground and surface mines and limestone quarries as well as urban areas, open grazing and grasslands (MDNR, 2008; Meneau, 1997). Uses of the Big River include irrigation, livestock watering, small-mouth bass fishing (upstream from mining sites), and recreational activities such as canoeing and floating (USEPA, 2015, 2021; MDNR, 2008).

Mining History

The earliest documented lead mine in the Big River area dates to the early 1700s and is believed to have been located near Old Mines, Missouri, slightly north of the current town of Potosi along Mineral Fork, a tributary stream to the Big River. French explorers recorded accounts of exposed outcrops bearing massive lead-zinc sulfide deposits near the Meramec

River, about 30 miles southwest of what is now the city of St. Louis (Eckberg et al., 1981; Hagni et al., 1989; Seeger, 2008). In the 1720s, Philippe François Renault, a French explorer, brought mainly French workers and black slaves with picks and shovels to mine surface and near-surface galena (PbS) and cerussite ($PbCO_3$) deposits near the towns of Potosi and Fredericktown (Hagni et al., 1989; Seeger, 2008). Several mining claims cropped up in the area and, during this time, lead production peaked at around 1,500 pounds of ore per day (Seeger, 2008). Much of the ore was transported down the river for processing, but some miners used rudimentary log furnaces to smelt the valuable metals into bars which were then hauled by cart to the Mississippi to be shipped to France and other regions for further purification and beneficiation (Eckberg et al., 1981; Seeger, 2008; USFWS, 2008).

The profitability of Missouri's lead resources fueled ambition, expansion and innovation. The arrival of Moses Austin in 1798 introduced more aggressive and productive mining practices. Austin directed more land-clearing, established a year-round mining operation including a mill and store, built roads and infrastructure for transport, and pushed for the industrialization of the area. However, despite better mining and smelting techniques, most of the minerals were still being harvested from surface deposits during the early 1800s (Fig. 8) (Eckberg et al., 1981, Seeger, 2008). At the same time, in Europe, the development and refinement of the diamond drill was being used to facilitate and accelerate railroad tunneling projects. The hollow, rotating casing was capped with a diamond encrusted bit and was originally patterned after ancient Egyptian stone-cutting technology (Burt, 2014). In 1869, the diamond drill was brought to Missouri by the St. Joseph Lead Company and was used for the first time in a mining exploration to locate profitable ore deposits in the Bonne Terre region (Burt, 2014; Hagni et al., 1989; Seeger, 2008). Over the next century deep shafts were sunk and

subterranean blasting created immense underground caverns supported by thick, undisturbed pillars of host rock. Extensive underground rail systems, over 400 km in total length, were constructed, connecting the Leadwood, Flat River and Elvins mines (Hagni et al., 1989; Seeger, 2008; Smith, 1988) (Fig. 9).

As the mining industry expanded throughout the late 19th and early 20th centuries, more efficient mining and beneficiation processes increased both lead and waste production. By the 1930's most of the lead mining claims were consolidated under the St. Joseph Lead Company (which later evolved into the modern-day Doe Run Company) and the entire region became known as the Southeastern Missouri (SEMO) Mining District (Hagni et al., 1989; Seeger, 2008; Smith, 1988). The District was divided into smaller subdistricts. Of these, three were world renowned for lead and zinc production: Old Lead Belt (OLB), Mine La Motte-Fredericktown, and the Vibernum Trend (VT).

Figure 8: Bonne Terre surface mining operations, 1866. Mining from shallow pits and surface deposits was the primary method of ore harvesting until 1869. Image source: www.rootsweb.com

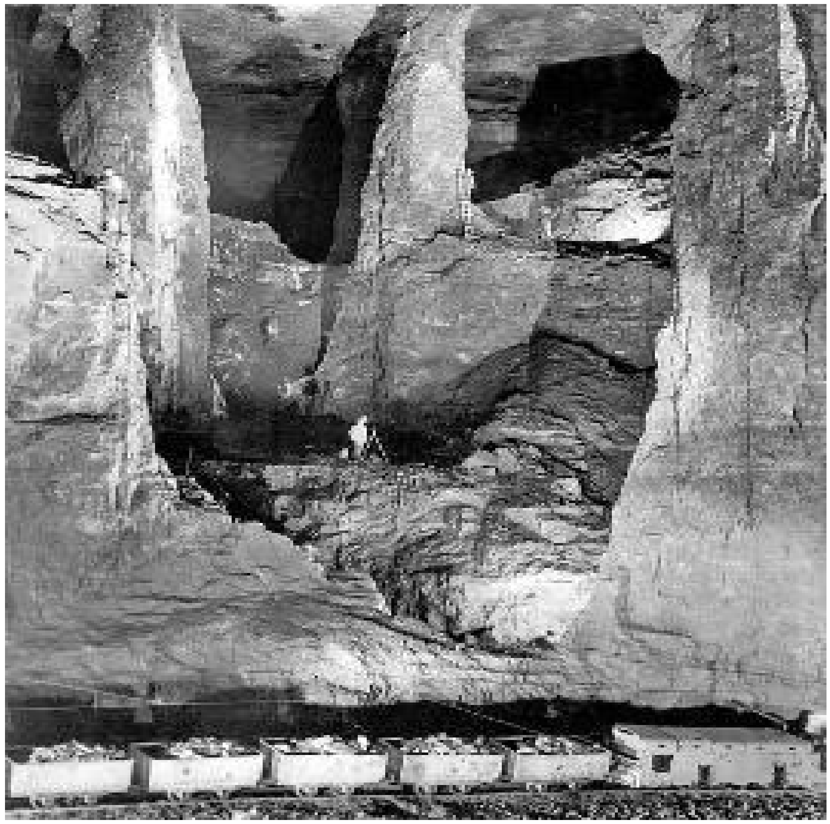


Figure 9: Typical room and pillar mining operation, circa 1940. Photo inside one of the first and most profitable deep shafts in the Bonne Terre district. Image: State Historical Society of Missouri - Digital Collections. Open-source photo titled “Federal No 11”.

Until 1964, the OLB was the leading producer (90% of SEMO production) of lead ore in the region, generating around 8.5 million short tons of lead over its entire active production (Mosby et al., 2009, Hagni et al., 1989; Seeger, 2008; Gerdemann and Myers, 1972; Pavlowsky et al, 2010). Other sulfide ore minerals, including sphalerite and chalcopyrite, provided zinc, silver, and copper (Gerdemann and Meyers, 1972). In 1940, exploration efforts revealed profitable ore deposits to the west and southwest of the OLB and by 1960 this new region became known as the Viburnum Trend (VT) sub-district (often referred to as the “New Lead Belt”) (Fig. 10).

Lead and zinc production in the VT soon surpassed all other sub-districts and by 1970, the SEMO mining district became the world leader in lead production, accounting for 15% of

worldwide lead production (Hagni et al, 1989; Seeger, 2008). Eventually, subsiding demand and declining profits prompted closure of the other, less productive sub-districts. By the mid-1970s, active mining had ceased in all SEMO sub-districts except the Viburnum Trend (Hagni et al, 1989), leaving behind a rich legacy of industry, capitalism, and community pride.

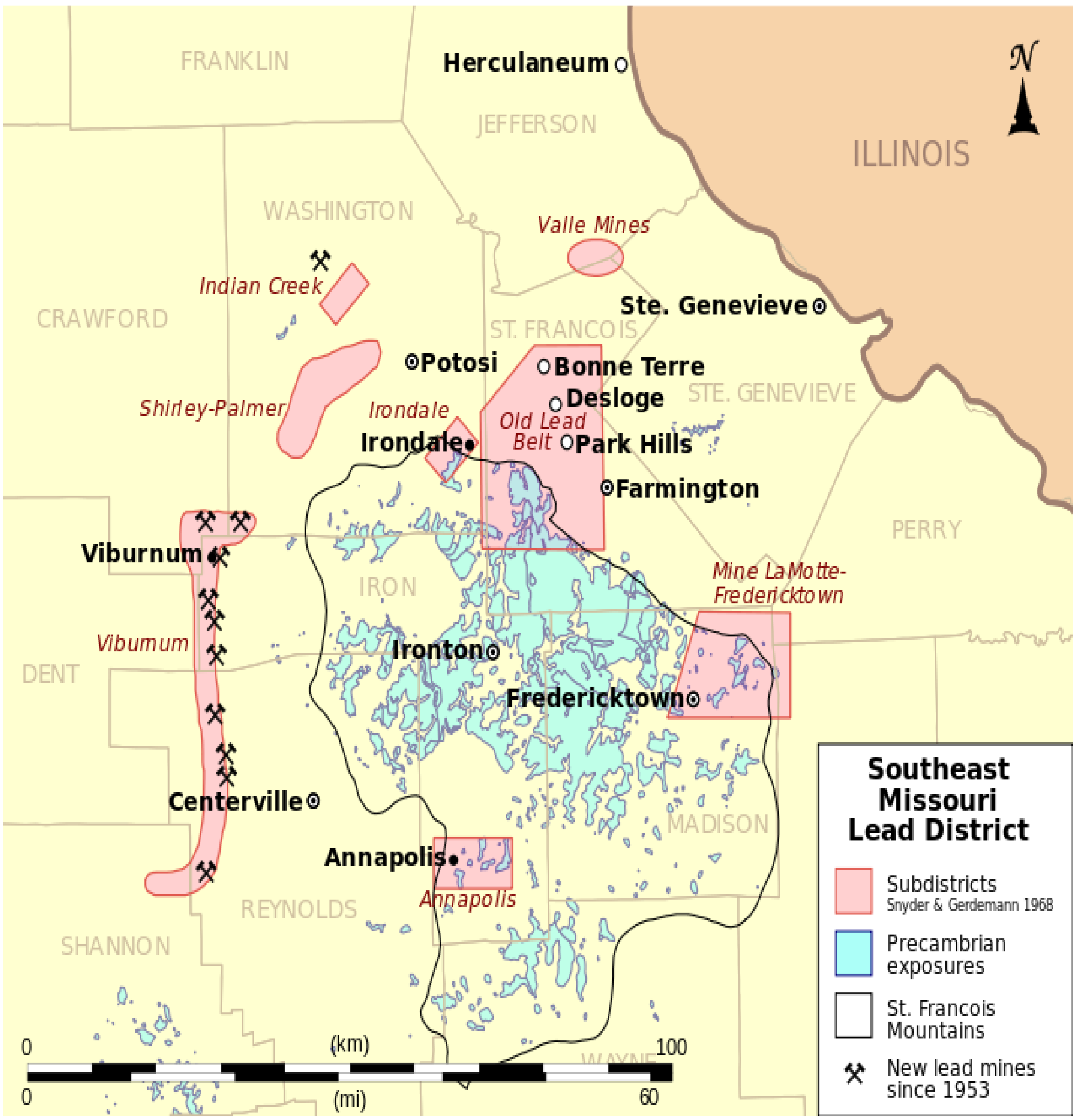


Figure 10: Map of Southeast Missouri (SEMO) Mining District and subdistricts.
Image: https://commons.wikimedia.org/wiki

Mine Sediment Texture and Appearance

Consistent with late 19th and early 20th century milling processes, the OLB produced milled sediments ranging from 16 mm to less than 0.25 mm (Pavlowsky et al., 2017). Coarse grinds (2-16 mm) from this region, locally called "chat" as described previously, are characteristically blue-grey in color, are typically derived from the Bonneterre dolomite, and exhibit an elongated, angular form due to milling processes (Fig. 11). Tailings analyses suggest that dolomite host rock fragments and smaller particles composed more than 95% of tailings pile material (Pavlowsky et al., 2010). Occasionally, small pieces of coal or metal slag from beneficiation processes are found deposited alongside mine wastes. The natural sediments in the area are mostly orange to brown pieces of irregularly shaped drusy quartz and chert, with the occasional occurrence of small, dark pieces of shale (Fig. 12). These natural sediments form most of the in-channel bed and bar deposits in the Big River. Most are derived from local outcrops and their abundance in the river is most likely indicative of earlier historical channel disturbance due to land use changes (Jacobson and Pugh, 1992).

Figure 11: Typical Old Lead Belt coarse tailing. Milling processes produced distinctively blue-grey, angular waste sediments.

Figure 12: Lithologic classification of grains in Big River channel sediments (4-8 mm). From left to right: A) natural sediment composed of chert and other silicate minerals, B) chat grains Bonne Terre dolomite from processed, and C) coal/slag pieces.

Environmental Legacy of Mining

In the OLB, mining and milling activities between 1864 and 1972 produced more than 7,300 Mg of Pb and generated over 226 million Mg of wastes which were stored in large above-ground piles or tailings impoundments (Schmitt and Finger, 1982; USEPA, 2007). These wastes still contained high residual Pb and Zn concentrations as metal recovery from historic beneficiation processes ranged between <80 to 95% (Pavlowsky et al., 2017). Close to 75% of the coarse, chat-sized tailings (2-16 mm) was repurposed as aggregate, fill, or liming agents, however, six significant piles remained near the Big River or its tributaries and were identified as areas of concern and added to the U.S. EPA Superfund: Leadwood, Desloge, National, Federal (St. Joe Park), Elvins/Rivermines, and Bonne Terre (Seeger, 2008; Pavlowsky et al., 2010;

USEPA, 2011) (Fig. 4 above). Actions to contain the waste included stabilization, regrading, capping and covering, and revegetation. As of 2016, remediation for all six piles have been completed (Pavlowsky et at. 2017; USEPA, 2021).

Leadwood Mine. The Leadwood mine was acquired and operated by the St. Joseph Lead Company from 1915 to 1962 (USFWS, 2008). The Leadwood tailings site, located near the town of Leadwood, MO, represents the most upstream location of mine activity on the Big River and is drained by Eaton Branch which enters the Big River just upstream from the Leadwood access on Hunt Street (MDNR, 2008). The chat dump began in 1904 and reached a height of just over 53 m (Karsch, 1973). In 1954 the quantity of chat at Leadwood was estimated around 8,200,000 Mg. Much of the chat was repurposed and redistributed throughout the community (MDNR, 2008). In 2006, Newfields (2007) determined the remaining volume approximated 3,900,000 m^3 for the tailings pile and Pavlowsky et al. (2010) estimated the pile covered an area around 2.3 km^2. Tailings samples from the Leadwood waste pile ranged from 597-17,000 mg/kg for Pb (average 2,382 mg/kg) and 400-25,800 mg/kg for Zn (average 4,691 mg/kg) (MDNR, 2008). Due to localized Zn enrichment in the OLB, mine sediments from Leadwood have the highest Zn content (average 5000 mg/kg) and thus produced a unique Pb/Zn geochemical ratio for Leadwood sediments ranging from 0.4 to 0.7 (Pavlowsky, et al., 2017). The Leadwood tailings site was stabilized in 2010 (https://cumulis.epa.gov).

Desloge Mine. The Desloge mine and mill was originally founded by Firmin Desloge in the late 1890s. The mill was built and began operating in 1893. Mined lead from the early years was shipped to Europe for use in the Napoleanic wars (USEPA, 2011; Desloge, 2012). St. Joseph Lead Mining Company purchased the mines in 1929 and mining continued at Desloge between 1929 and 1958 (USEPA, 2011). Wastes were transported to the Desloge tailings pile,

which was located on the banks of the Big River within a large meander bend just downstream from Owl Creek, from 1894 until 1931 (USFWS, 2008; Smith, 1988; Karsch, 1973). The area of the pile covered around 2.3 km^2 (Pavlowsky et al., 2010). Tailings from the Desloge area had an average lead content of 2,105 mg/kg and around 1,200 mg/kg for zinc (Newfields, 2007; Pavlowsky et al., 2017). In 1977, approximately 38,000 m^3 of contaminated tailings slumped into the Big River from the Desloge site as heavy rains compromised the stability of the storage site (USEPA, 2012; Schmitt and Finger, 1982). The steep slopes of the piles and undercutting by the Big River delivered additional material to the river until it was stabilized in the autumn of 2000. There are ongoing efforts to revegetate the area (Smith, 1988; MDNR, 2010).

Bonne Terre Mine. Organized mining in the OLB area began at the Bonne Terre mines around 1864. After fires destroyed the millworks 1883 and 1884, the operation was purchased by St. Joseph Lead Company. Ores were transported for processing to the Herculaneum smelter after its construction in 1892 and mining ceased in 1961 (USEPA, 2011; Smith and Schumacher, 1991). The chat pile was used from 1918 until 1931 (Karsch, 1973). The pile and tailings pond covered about 1.4 km^2 and were located close to the Big River, near the junction of U.S. Hwy 67 and State Hwy K about 3 kilometers west from R-km 145. The Bonne Terre waste sites are mainly drained by Turkey creek, which joins the Big River near R-km 136. Removal and remediation of the site concluded in 2007 (MDNR, 2008; Pavlowsky et al., 2010).

Federal Mine. The Federal mill was built by the Federal Lead Company around 1906 (OzarksWatch, 1992). The site was acquired by the St. Joseph Lead Company in 1923 and mining and milling activities continued until the mine's closure in 1972. The Federal site was the last to close in the Old Lead Belt (USFWS, 2008; Smith, 1988). The coarse tailings pile was used between 1907-1931, grew to about 94m, and was located within what is now known as the

Missouri Mines Historic Site in Park Hills, MO (MDNR, 2008; Karsch, 1973). With the development of more efficient recovery methods, many of the coarse tailings from the pile were reprocessed and redeposited as slurries into natural depressions. The chat and tailings covered around 4.7 km^2 (Newfields, 2007; MDNR, 2008). An additional tailings pond was created in 1947 by an impoundment of Davis Branch (now known as Shaw Branch), which drains into Flat River Creek. The tailings were poorly contained and, around 1950, the impoundment failed. The lower portion of Shaw Branch was almost completely buried under tailings (MDNR, 2008, 2010). MDNR (2008) estimated around 268,000 m^3 of contaminated wastes were released from the impoundment throughout its history and, in 2006, an estimated 7,600 to 23,000 m^3 still remained in Shaw Branch. Stabilization of the Federal area was completed in June, 2021 (https://cumulis.epa.gov).

National Mine. The National waste rock and tailings piles were located north of the town of Park Hills, MO, near the Flat River railway station on the Mississippi River and Bonne Terre railroad. Mining activities were already underway when the site was purchased in 1898 by a subsidiary of the National Lead Company (USEPA, 2011), consolidating the previous small mining operations. In 1901 a small electric mill was constructed. The chat pile was started in 1904 and wastes were generated on-site during mining and milling activities until the mine was purchased by St. Joseph in 1933 (Karsch, 1973). After purchase, ore was hauled underground to Federal mill for processing (USEPA, 2011). The site contained around 0.6 km^2 chat and tailings and stabilization of the pile was completed between 2006 and 2012 (Pavlowsky et al., 2010; USEPA, 2011).

Elvins/Rivermines. The waste pile from mining activities is located near the former towns of Elvins and River Mines and within the current city of Park Hills. Mining and milling

operations began in 1890 and continued at this location until 1940 (USHHS, 2004; USFWS, 2008). The pile, used from 1909 until 1939, was approximately 52 meters high and covered around 20 acres (Karsch, 1973). The site also included a tailings pond north of the pile. Historically an asphalt plant and quarry sold tailings to farmers as agricultural lime and used coarse material (chat) in their asphalt mix (USHHS, 2004). The average lead content in tailings from the waste pile ranged between 1177 to 9283 mg/kg. Remediation of this pile included regrading and capping the pile and removing tailings from the spillway and creek channel and the site was stabilized in 2006 (USHHS, 2004; MDNR, 2010).

METHODS

Site Selection and River Measurement

Length in the Big River was measured in river kilometers (R-km) beginning at the confluence with the Meramec (R-km 0) and ending at Council Bluff Lake (R-km 220) (Owen et al., 2012; Pavlowsky et al., 2010, 2017). As described previously, the USEPA and MDNR have been engaged in efforts to manage the consequences of contaminated sediment releases from waste piles to the Big River during much of the 20th century. Smith and Schumacher (1991, 1993) conducted a comparison of control and mining input sites on the Big River which showed local, natural dolomite outcrops did not contribute significant carbonate sediments to the sediment load. In contrast, sediment samples from chat piles and tailings sites were typically composed of 100% dolomite (Pavlowsky et al, 2010, 2017; Newfields, 2007; MDNR, 2010). Therefore, it can be assumed that dolomitic bar sediments in the Big River originated from mine inputs.

The presence of coarse tailings (chat) in the channel presents an ongoing concern due to their high residual Pb and Zn content (MDNR, 2008). Preliminary analysis of in-channel sediments in mine-affected reaches showed varying Pb concentrations by size fraction with around 5,000mg/kg Pb in chat sizes (4-8 mm), 2,500 mg/kg for <2 mm sediments and >10,000mg/kg in slimes (<63µm) (Pavlowsky et al, 2010). Further, Pavlowsky et al. (2010) detected high dolomite presence in coarse (2-16 mm) bar sediment samples between Leadwood and Bonne Terre which appeared to taper off by Highway E (R-km 132.9). Besser et al. (2009) and Pavlowsky et al. (2010) found elemental Pb and Zn levels above the PEC in pore-water and very-fine sediments between Leadwood (R-km 171) to the confluence with the Meramec River,

with the highest levels of Pb occurring between the Bone Hole (R-km 165.3) and Hwy E (132.9). Pavlowsky (2010, 2017) used elemental Ca percentages as sediment tracers to indicate the presence of mine waste in the river. These studies showed dolomite presence in channel sediments was significant near mining input sites and elevated elemental Ca levels were detected in fine sediments downstream from mining inputs as far as Morse Mill (R-km 50).

As a result of these findings, as well as information from studies by MDNR (2010) and Owen et al. (2012), the following tributaries were identified as significant point source inputs: 1) Eaton Branch, which drains the Leadwood pile (R-km 171), 2) Desloge pile slump (R-km 164), 3) Flat River, which drains National, Federal, and Elvins/Rivermines piles, and 4) Turkey Creek, which drains the Bonne Terre pile and tailings pond. Other significant locations that may have affected 2013-14 sediment storage and distribution include three low-water crossings, road and railroad bridges, the Bone Hole dredge site (R-km 165.3) and bar excavation site (R-km 163.4), and two state parks: St François State Park (R-km 143 to 138), and Washington State Park (R-km 100) (Table 2). To expand and refine the initial data set obtained by Pavlowsy et al.(2010), gravel bar sample sites were identified for further sampling approximately every 400 meters within a 70-km region of interest beginning at the Big River Leadwood access (R-km 170.7) and ending at Washington State Park (R-km 101) (Fig. 13).

Field Methods

Sample collection. In the Big River study area, a total of 172 samples were hand-collected from in-channel gravel bar sites approximately every 400 meters downstream from the Leadwood access (R-km 170.7) to Washington State Park (R-km 101.7) (Table 2). From June 12-14, 2013, 89 bar samples were collected between the Leadwood access point to state Hwy E

(R-km 133), where previous research indicated a significant increased dolomite presence (Pavlowsky et al., 2010). From July 8-9, 2014, an additional 84 samples were collected between Hwy E (R-km 133) and Washington State Park (R-km 101.7). In 2013, multiple flooding events occurred within the 6 months prior to sample collection. Sediment distribution may have been affected as maximum water levels occurred at a gauge height of 7 m (23 ft) in May, just over 2 meters above minor flood stage (https://waterdata.usgs.gov; https://water.weather.gov) (Fig. 14). Slumping and significant woody debris were noted in many areas. One minor flooding event also occurred in April, 2014 with maximum gauge height at 5.1m (16.8 ft).

To address the effects of selective sorting on the surface and more accurately represent long-term bar storage and metal content of the sediments, samples were collected below the lag/pavement layer, at an average depth of 15-20 cm, with a small shovel, immediately stored in quart-sized freezer bags, and labeled by river kilometer (Pavlowsky et al., 2010). GPS coordinates for 2013 sample locations were obtained using Google Earth and 2013 NAIP georeferenced shapefiles in ESRI's ArcMap 10.6. In 2014, GPS coordinates were obtained using a Nikon CoolPix AW110 GPS camera.

Channel measurements in both 2013 and 2014 included bar height, bar type, bar location within the river, sample location within the bar (head, middle, tail) and water depth at the deepest location near the bar. Appendix A contains both channel and GPS measurements for each bar sample. For quality assurance, in both 2013 and 2014 duplicate field samples were collected around every 4-5 sampling sites from the same bar location. Additionally, in 2014, a sample of coarse tailings (chat), originating from the Federal Mine chat pile and assumed to have remained outside the fluvial environment, was obtained from the Missouri Mines State Historic site for petrographic analysis.

Table 2: Big River significant locations (*After Pavlowsky et al., 2010)

River-Km (R-km)	Location notes
171	Eaton Creek tributary
170.7	Leadwood access – Low-water bridge at Hunt St.
165.3	Bone Hole excavation site – Owl Creek tributary and low-water bridge
165-156	Desloge waste pile site (meander bend)
163.4	Borrow pit bar excavation site (Owen et al., 2012)
158.1	Old Bonne Terre Rd Bridge
156	U.S. Route 67 bridge
155	Flat River Tributary
147.1	State Route K bridge
144.5	Terre Bleue Creek Tributary
143	St. François State Park
136.7	US Route 67 bridge
136	Turkey creek tributary
134.5	Bee creek tributary
132.9	State Route E bridge
132.5	Cabanna Course tributary
121.1	Dickenson Rd low-water bridge
118	Mill Rd. bridge
115.5	Mill Creek tributary
115	Hwy CC bridge
107	State Route 21 bridge
101.7	Washington State Park

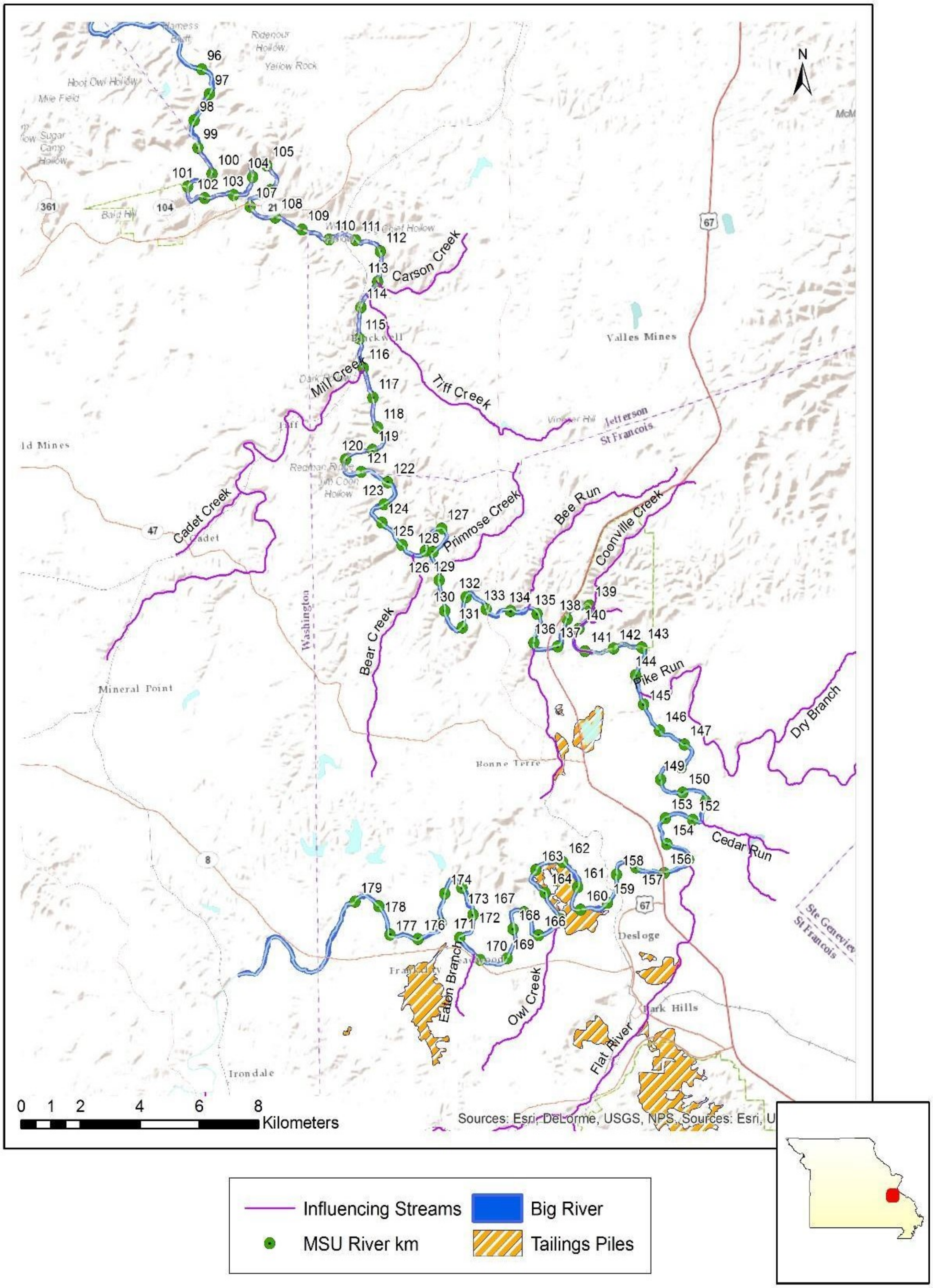


Figure 13: Big River study area.

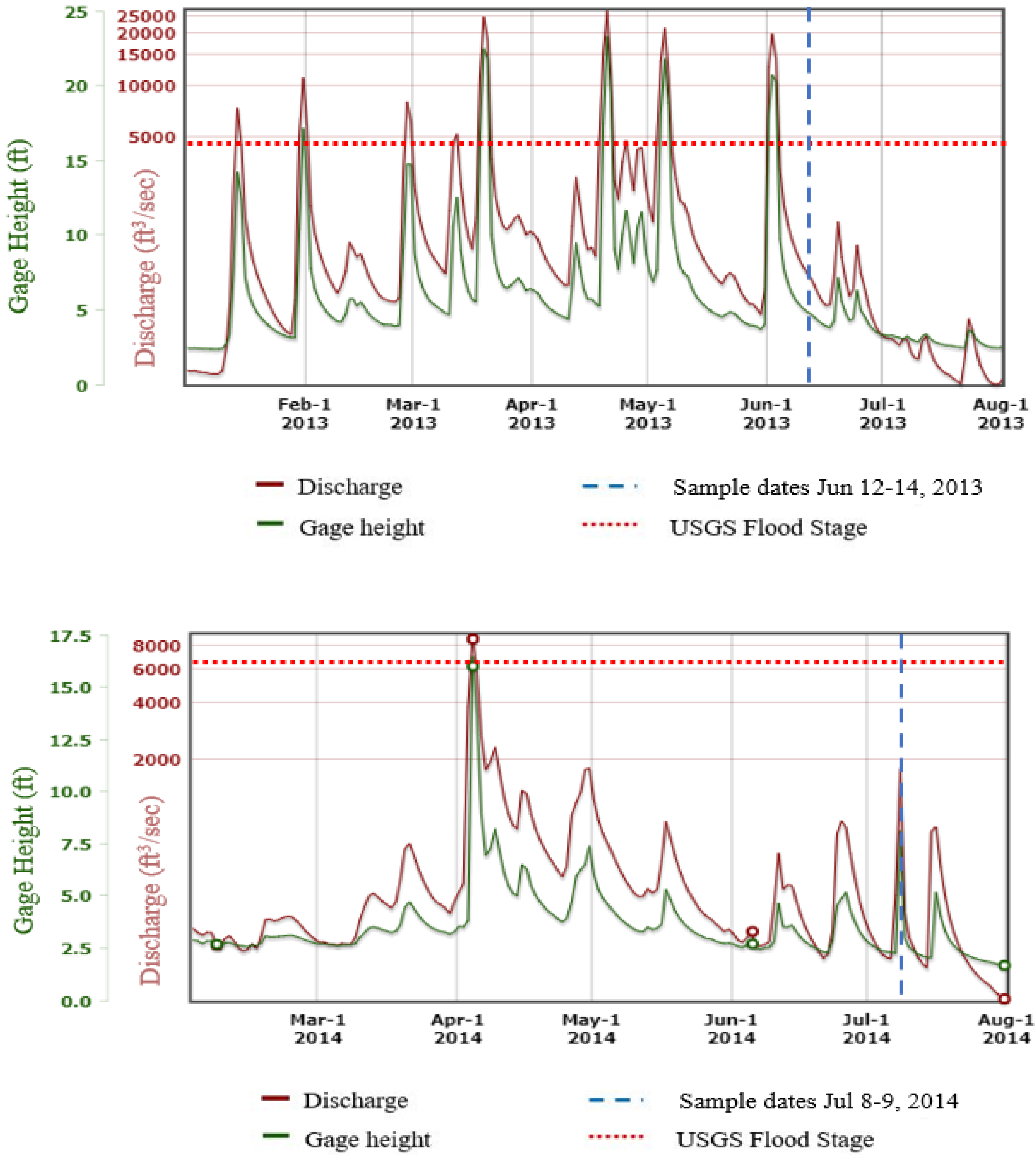


Figure 14: USGS Big River stream gage data at Byrnesville. **A.** Feb – Aug, 2013. Multiple high-water events occurred with maximum gauge height of 7m (23 ft) in the 6 months prior to sample collection dates, June 12-14, 2013 (marked). **B.** Mar – Aug 2014. One minor flooding event occurred in April, 2014 with gauge height at 5.1m (16.8ft). Data and charts modified from https://nwis.waterdata.usgs.gov.

Laboratory Methods

Sample preparation. Sediments were oven-dried at 60º C until all moisture was removed, after which each sample was measured for total mass in grams. Samples were sieved into >32 mm, 16-32 mm, 8-16 mm, 4-8 mm, 2-4 mm, and <2 mm size fractions, weighed, and stored in labeled Ziploc bags (Fig. 15). Sediments >32 mm were measured and noted but excluded from further evaluation since the target mining wastes for this study do not typically occur in sizes greater than 16 mm. Also, some samples contained shells, twigs, and/or other irrelevant material which were removed. This accounts for slight variances between original sample weights and totaled size fraction weights (Pavlowsky, et al. 2010, 2017). Sample weights for all bar samples were stored in an Excel workbook and are available in Appendix A.

Figure 15: Processed Big River channel bar samples.

Geochemical analysis. Smith and Schumacher (1993) found that Big River bed-sediment in downstream mining sites contained more calcite and dolomite, while areas unaffected by mining contained mainly quartz. Additionally, OLB mine wastes were reported to contain high levels of Pb and Zn (MDNR, 2008; Newfields, 2007; Pavlowsky et al., 2010). Therefore, to refine the data in the mine-affected areas, elemental concentrations of Ca, Pb, and Zn for small (20-30 g) subsamples of the <2 mm and < 0.25 mm sediment fractions for each sample location

were determined by X-ray fluorescence (XRF) using a handheld X-MET 3000TXS+ model by Oxford Instruments. In some bar locations, only about 5-10 g of <0.25 mm sediment was able to be collected from a specific bar location sample and XRF analysis was completed by carefully positioning the bagged sample over the detector. Chain of Custody (COC), standard operating (SOP), and quality assurance (QA) procedures for handling and analysis of sediment samples were followed according to the standard methods used in the soil laboratory at the Ozarks Environmental and Water Resources Institute (OEWRI) at Missouri State University (https://oewri.missouristate.edu/).

Residual Ca, Pb, and Zn concentrations in gravel-sized (2-16 mm) chat and natural sediments were also determined using XRF. Subsamples of isolated chat and natural sediment grains were picked from the sieved 2-4, 4-8, and 8-16 mm size fractions from ten random bar location samples. Each subsample was cleaned with a sonic cleaner and ground to < 0.25 mm using a ball-crusher. The crushed sediments were stored in Ziploc bags, labeled, and analyzed using the handheld X-MET 3000TXS+. The ball crusher was carefully cleaned between samples to remove any residual material. While both <2 mm and <0.25 mm samples were analyzed for a broad spectrum of elemental content, only Pb, Zn and Ca were evaluated for this study. Previous environmental assessments and research in the Big River considered Cd levels, however, this study's focus specifically aims to identify the presence of mine waste in channel deposits which have been correlated to elevated Ca, Pb, and Zn levels. Additional elemental results, including Fe, Mn, and Ti, are available in Appendix B.

Thin sections. Grain mount thin sections were prepared for petrographic analysis from a sample of 4-8 mm chat grains obtained from the Missouri Mines State Historic site. The chat grains originated from the Federal mine chat pile and, to the author's knowledge, may have been

subject to intermittent weathering during storage in chat piles but were not exposed to direct in-channel fluvial processes. The grains were highly angular and showed few signs of weathering. They were sonically cleaned and rinsed in de-ionized water, then stabilized in a thick layer of standard epoxy on a base slide. The exposed side of the grains were cut, wet-polished with 240 and 600-grit until level, and again cleaned with a sonic cleaner. A second base slide was attached to the buffed side using the same mounting epoxy. The first slide was then cut away with a diamond saw to expose the other side of the grains. This side was also wet-polished with 240 and 600-grit to ~32 um and a top slide was applied (Fig. 16). For a more detailed description of this method see Carver (1971). The thin sections were analyzed and photographed using a Leitz Wetzlar 633554 binocular petrographic microscope.

Figure 16: Petrographic slide sample of 4-8 mm chat grains from Federal Mines area.

Computational Methods

Bulk Mass Percent by Size Fraction. For each gravel bar sample, <32 mm bulk mass percentages were calculated by dividing the measured mass of each size fraction by the total mass of the sample (less removed >32 mm and irrelevant material). Mass percentages for

sediments <0.25 mm were calculated as follows: 1) the subsample weight percentage was calculated by dividing the sieved <0.25 mm XRF sediment weight by the weight of the <2 mm subsample from which they were taken; 2) the total <2 mm weight for the sample was then multiplied by the <0.25 mm percentage to calculate the <0.25 mm sediment mass and percentage of the entire sample; 3) the total <0.25 mm sediment sample mass was subtracted from the total <2 mm sediment sample mass in order to calculate the mass and percentage of 0.25 – 2 mm sediment size fraction. Results for mass percentages for each sample location in each size fraction are available in Appendix C.

Bar Sample Lithology Percentages. Chat abundance in gravel bars was quantified by using grain counts of different sediment types within a specific size fraction according to color and lithology, similar to Pavlowsky et al. (2010, 2017). **S**ubsamples of 100-150 grains were randomly picked from each size fraction and sorted into the following classes: dolomite, natural sediment (quartz, chert, etc.) and coal/slag. As described earlier, processed Old Lead Belt MVT sediments were mainly mined from the Bonne Terre formation and occurred almost exclusively as angular, blue-gray to light tan fine-grained dolomite chips (Smith and Schumacher, 1993). Natural sediments, typically derived from local outcrops, constituted most of the in-channel bed and bar deposits. These included tan, orange and brown pieces of irregularly-shaped drusy quartz and chert, with the infrequent occurrence of small, dark pieces of shale. Although most of the characteristic crystallized coating associated with drusy had been removed due to weathering in the river, some was still present. Some natural sediments may have been subjected to milling processes; however, limited sampling of chat-sized tailings indicated an insignificant presence of silicates in piles from several different waste sites (Pavlowsky et al., 2010). Small, black pieces of coal and slag, including cinders and residual flux from smelting and refining processes,

exhibited vesicular and brittle textures and were present and indicative of mining activities. (Smith and Schumacher, 1993; Pavlowsky et al., 2010, 2017) (Figs. 17 A-C and 18).

Separated subsample grains were counted and lithology percentages were calculated by dividing the number of dolomite or natural grains by the total number of grains counted. Lithology counts and percentage calculations are provided in Appendix D. Duplicate lithology counts (to account for operator error) were conducted for 14 bar samples, yielding precision measurements of around 2%. Pavlowsky et al. (2010) noted shale/slag percentages in bar deposits. Although coal and slag sediments most likely originate from smelting operations, their occurrence is relatively infrequent, and they do not necessarily affect sediment heavy metal concentrations. Therefore, to narrow the focus on the presence of dolomite vs. natural sediments for this study, the coal/slag counts were added to the natural/other count. However, the results including the coal/slag counts and percentages are available in Appendix D.

Fine Tailings Composition Using Calcium as a Tracer. Sulfide ores in the SEMO mining district are mainly hosted in dolomitic facies (Gregg, 1985). Mine waste sediments are primarily composed of dolomite while natural sediments in the Big River are mainly quartz (Newfields, 2007). When analyzing mixed channel deposits of mine-affected regions, the presence of high Ca concentrations can indicate the presence of carbonates, and therefore, mine-related wastes (Adams, 1944; Macklin et al., 1994; Pavlowsky et al, 2010, 2017). Pure dolomite averages around 217,000 mg/kg Ca and previous studies reported Ca levels from control sites upstream of the mine-affected study area averaged between 3,500 to 6,400 mg/kg (Pavlowsky et al., 2010). By subtracting the background levels (3,500 mg/kg) and dividing by the pure Ca content of dolomite, an estimate of the tailings presence in the <2 and <0.25 mm size fraction was produced.

Figure 17A: Coarse “chat” grains. Blue-gray limestone chips are typical from the Bonne Terre formation and exhibit angular shapes due to milling.

Figure 17B: Natural gravel bar sediments. Typical natural sediments include weathered orange to brown chert and drusy quartz pieces.

Figure 17C: Coal/slag sediments. Coal and slag are left over from beneficiation processes and are deposited alongside natural and dolomite grains.

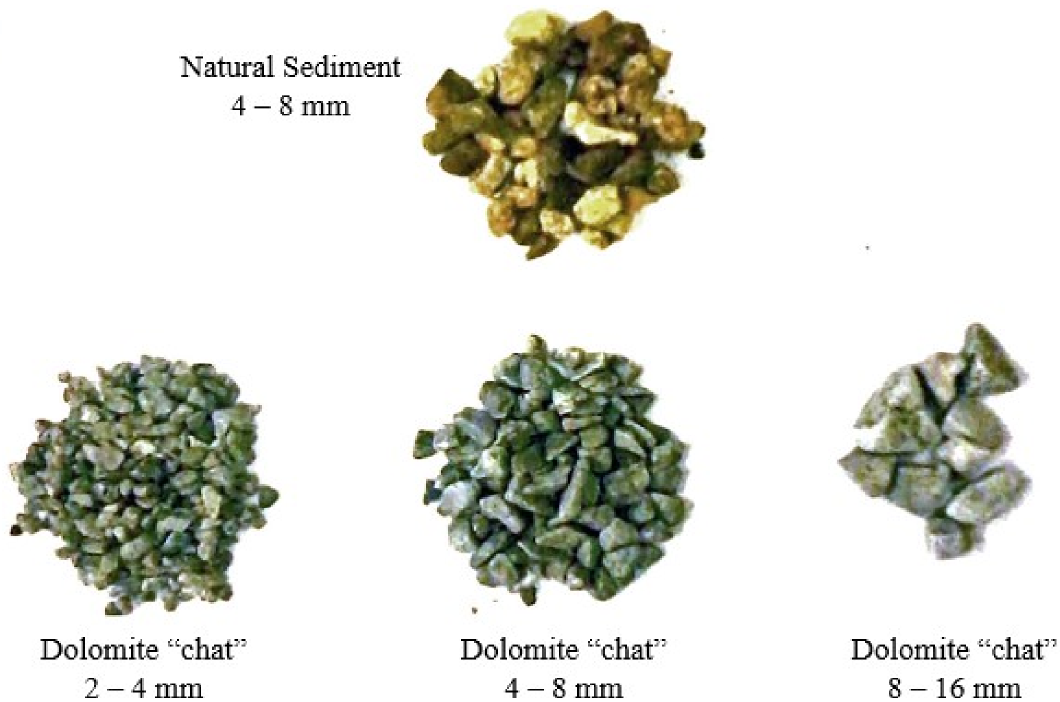


Figure 18: Dolomite chat size fractions in Big River bar deposits. Natural (chert/quartz) sediments are shown in contrast to the dolomite waste sediments.

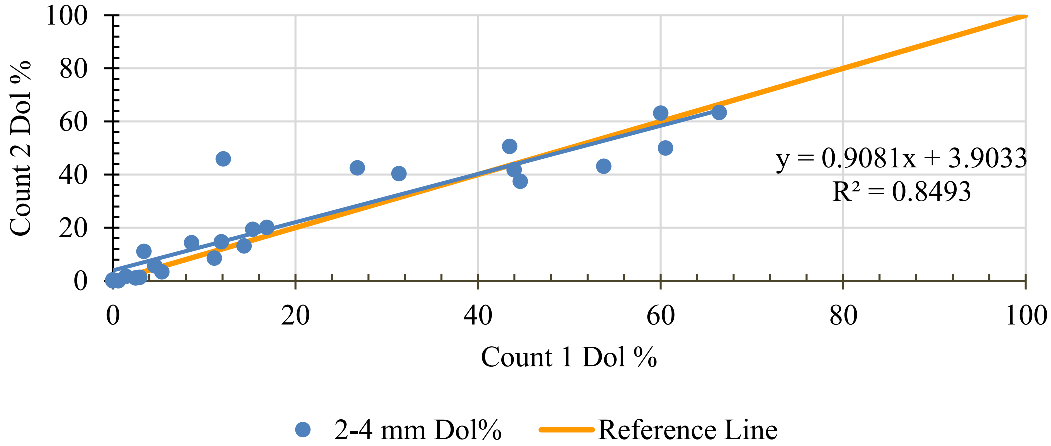
Quality Assurance (QA)

Field duplicates are defined as additional samples collected in the field from the same gravel bar location and river kilometer. A total of 24 field duplicates were collected, every 4-5 samples, and analyzed to show homogeneity in lithology distribution within the bar. Differences between field samples would have indicated the bar was not well-mixed and was not a good representative of the bar as a whole. Lithology percentages were calculated for duplicate field samples in each size fraction and compared. Due to the downstream decline of dolomite in the bar samples, percent difference calculations did not provide a good representation of accuracy as percent difference results became skewed as the mean approached zero. However, the average of

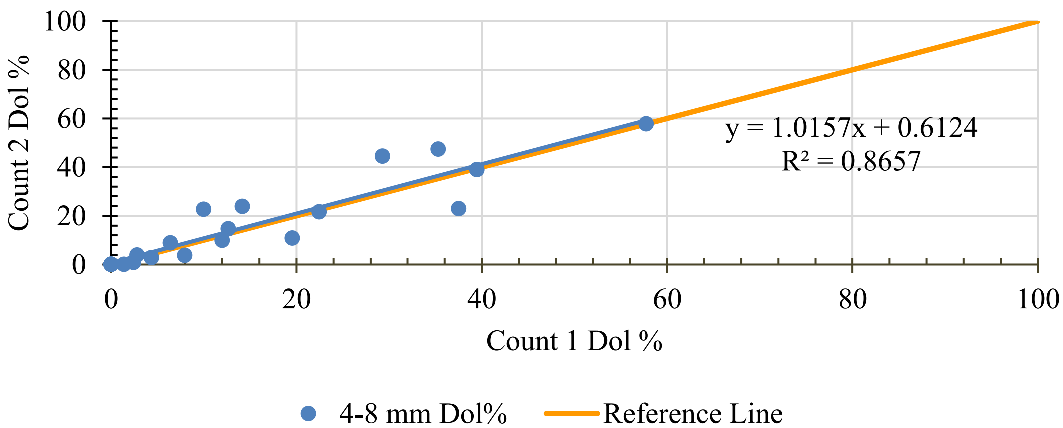
total differences between field duplicate counts was around 4%. When field duplicate results were plotted against a 1:1 line they showed high precision (±10%) in lithology counts (Fig. 19).

Duplicate lithology counts were performed for 14 samples in 2-4 mm, 25 samples in 4-8 mm, and 17 samples in 8-16 mm size fractions. After the initial subsample pick and percentage calculation from the sieved size fraction within a bar sample, an additional subsample (100-200 grains) was picked, counted and lithology percentages were calculated. This was used to show precision in calculation of the lithology percentages for the individual gravel bar samples and variations would have reflected the amount of mixing in the sample. A low difference between percentages indicated a good representation of the mixing of the sample as a whole. As with the field duplicates, percent differences for these duplicate counts were skewed due to the low mean values in samples that had minimal dolomite presence. The average total difference between counts was around 4.4%. Like the field duplicates, the results for lithology count duplicates were also plotted against a 1:1 line and also showed high precision results (±10%) (Fig. 20).

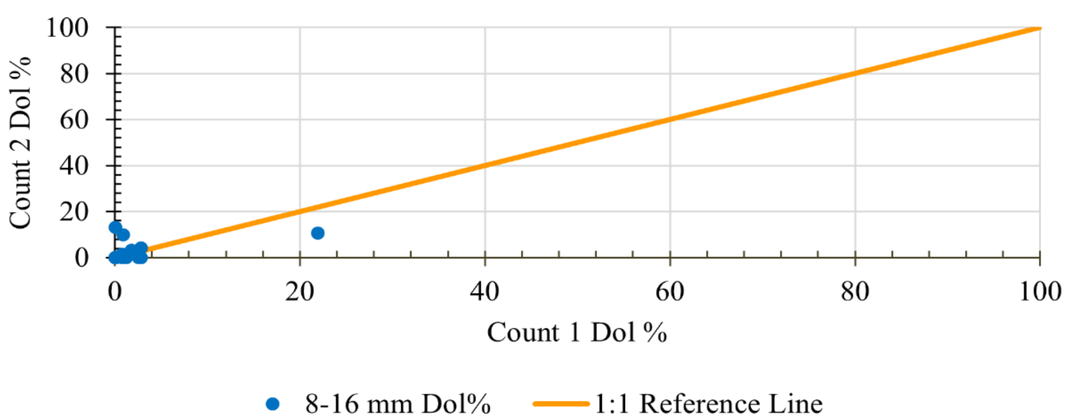
Lab duplicates are defined as duplicate XRF scans conducted every 10 samples on the sieved and separated <2 mm and <250 um samples to demonstrate precision in XRF readings. Standard quality control procedures, including scanning blanks and soil check standards were performed according to OEWRI standard operating procedures (https://oewri.missouristate.edu). Relative percent difference values averaged around 10% with CV% close to the same. Aqua Regia analysis was conducted by Chemex Laboratories for 23 subsamples to clarify elemental concentration measurements. Raw XRF results for both 2013 and 2014 samples were corrected to adjust for actual concentration by multiplying raw results by the following adjusted ratios: 1.09 (Pb), 1.27 (Zn) and 0.74 (Ca) (Pavlowsky et al., 2017).



A.

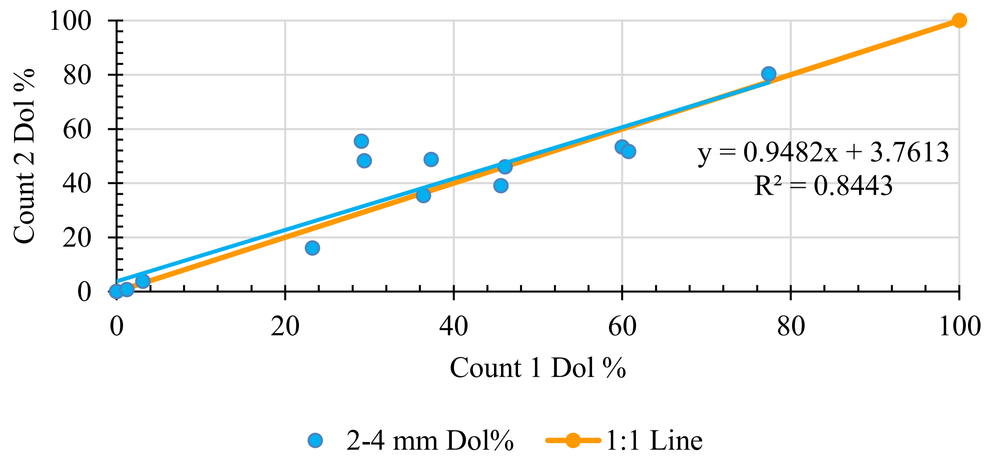


B.

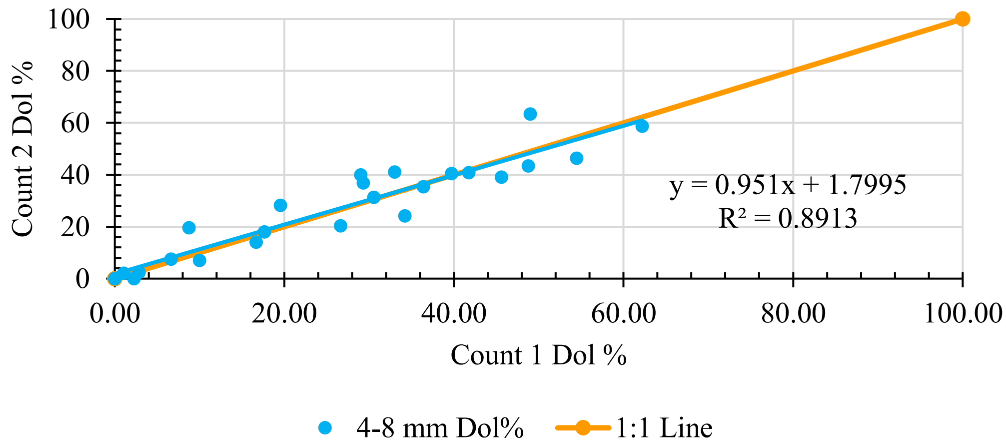


C.

Figure 19: Bar sample variability. Duplicate field counts were plotted against 1:1 line by size fraction. Results for 8-16 mm limited by abundance in the sample.



A.



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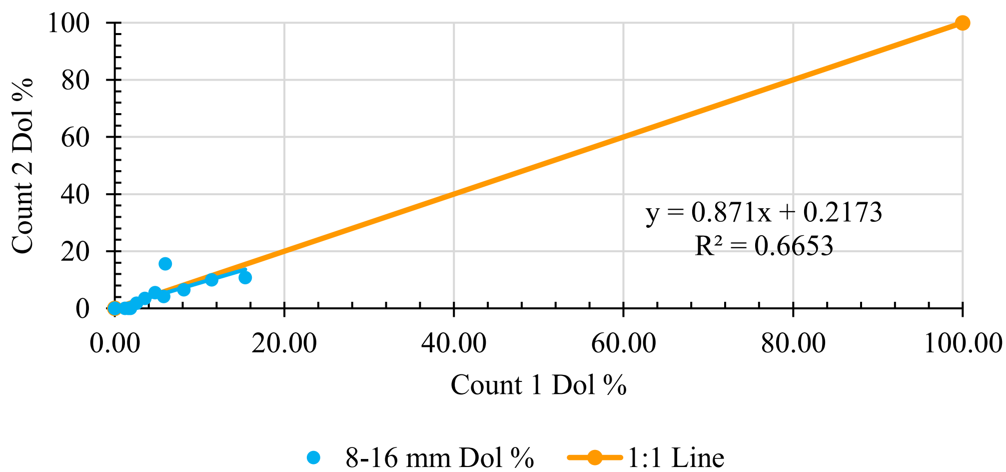


C.

Figure 20: Precision in dolomite percentages. Duplicate dolomite percentages calculated from different picks from the same sample bag. Dolomite percentages were plotted against a 1:1 best fit line for each size fraction as shown in figures A, B, and C.

Geographic Information System (GIS) Methods

Maps in this report were created using ESRI ArcMap 10.6. Shapefiles for cities, streams, states, counties, river kilometers, waste piles and Big River active channel were obtained from the OEWRI geodatabase and modified by the author. To create a spatially accurate sample point feature, 2014 sample GPS coordinates were imported into ArcMap using the GeoTagged Photos to Points tool. Additional points were created for the 2013 samples by importing the decimal degree latitude and longitude coordinates into the geodatatable for each sample. Correct point locations were verified by importing the georeferenced river kilometer point feature into Google Earth and comparing marked field maps to historic satellite imagery. Bulk and lithology percentages, as well as measured Pb, Zn, and Ca levels were used to create a geodatatable and then imported as field values into the study sample points feature.

RESULTS AND DISCUSSION

This study evaluated the sediments <32 mm in diameter within Big River gravel bar deposits with the following objectives: 1) quantify and refine the understanding of the abundance, distribution, and downstream dispersal of coarse mine waste particles (2-16 mm) below mine waste input sites, 2) analyze Ca, Pb, and Zn concentrations in fine (<2 mm) bar deposit sediments, and 3) evaluate the ongoing contamination role of “chat” (coarse mine wastes 2-16 mm) for in-channel bar deposits. This chapter provides 1) size trend observations in overall sample bulk composition downstream from mine sediment inputs, 2) the observed downstream spatial trends related to sediment size and lithology, 3) quantified metal distributions in fine gravel bar sediments and their geographic distribution, and 4) analysis of the chat particle composition and their possible role in future, ongoing contamination of the Big River.

Sediment Size Bulk Distribution

As described in the Methods section, Big River bar samples <32 mm were sieved into the following size fractions: <0.25 mm, <2 mm, 2-4 mm, 4-8 mm, 8-16 mm, and 16-32 mm. For each sample, the bulk percent composition percentages for each size fraction was determined by dividing the weight of each size fraction by the total weight of the sample and multiplying by 100%. Also, recall that tailings input sites on Big River included the Eaton Creek Tributary (R-km 171), which drains the Leadwood pile, the Desloge Tailings site (R-km 166-160), the Flat River Creek tributary (R-km 155), which drains the Federal, National and Elvins/Rivermines tailings sites, and the Turkey Creek tributary (R-km 136), which drains the Bonneterre site (see Table 2 in previous section).

When evaluated by channel segment, the highest average bulk percentages for chat-sized sediments (4-16 mm) were observed at just below 21% in the first mine-affected reach, between Leadwood (R-km 171) and Flat River (R-km 155) but also exhibited high variability between bar deposits (Table 3). The mean bulk percentage for the 2-4 mm size fraction peaked near 19% in the second segment, between Flat River Creek and Terre Bleue Creek. Average segment values for all size fractions declined with distance downstream to Cabanna Course (R-km 132.5). Between Cabanna Course and Washington State Park (R-km 102), there was a slight increase in average bulk percentage in the 4-32 size fractions while the average percentages in the 2-4 mm and <2 mm size fractions continued to decline (Table 3).

Table 3: Average sediment size distribution percentages by river segment. Shown for Big River bar sediment samples <32 mm in diameter.

			Size Distribution (%) (in mm, with <32mm = 100%)					
Segment	**n**	**Value**	**16 - 32**	**8 - 16**	**4 - 8**	**2 - 4**	**0.25 - 2**	**<0.25**
1	38	Mean	11.3	16.7	20.5	16.5	31.5	3.3
171-155 R-km		CV%	65	34	28	37	31	56
2	21	Mean	7.3	11.5	18.8	18.7	40.4	2.9
155-144.5 R-km		CV%	78	68	44	33	51	63
3	26	Mean	7.6	10.9	14.8	14.9	47.6	3.8
144.5 - 132.5 R-km		CV%	82	49	43	48	37	65
4	36	Mean	8.7	13.8	14.2	12.3	47.0	3.7
132.5 - 115.5 R-km		CV%	75	40	43	44	29	86
5	29	Mean	11.5	16.8	15.5	11.4	40.8	3.6
115.5 - 102.1 R-km		CV%	57	32	30	30	30	79

Throughout the study area the <2 mm size fraction dominated the average bulk percent composition and showed a wide range of individual bar deposit bulk percentages, varying between 10% to over 90% (Fig. 21). Using a five-point moving average, peaks near 70% for <2 mm sediments were reached around the Turkey Creek Tributary (R-km 136) and again just above Mill Creek (R-km 115.5). By the end of the study area, at Washington State Park (R-km 101), the <2 mm sediment percentage average was still above 40% of the bar deposit bulk composition. Within the <2 mm sediments, the <0.25 mm fraction constituted an average of less than 5% of the total bar composition. The low amounts of very-fine material were not unexpected, as the <0.25 mm fraction typically remains suspended during transport and continues traveling farther downstream. Peaks in this size fraction occurred near R-kms 135, 127, and 120 and are likely indicative of local variances in stream energy and morphology (Huggett, 2011).

The five-point moving averages for the 8-32 mm sediment bulk percentages show simultaneous peaks and lows throughout the study area (Fig. 22). It is likely that stream dynamics represent the largest control in where these sediments are being deposited. The overall increase in <2 mm and 2-16 mm sediments below near the Flat River tributary (R-km 155) may reflect an influx of released waste particles from the Federal, National, and Elvins/Rivermines waste piles (Pavlowsky et al., 2010) (Figs 21 and 22). Downstream from the Flat River confluence, bulk percentages for all <32 mm size fractions fluctuated widely, with highs manifesting in discrete bar locations. This suggests the main bulk of these sediments may be affected by local variations in transport rates and sediment sources, may be moving in slugs or pulses, may represent "hot spots" controlled by geomorphology and stream energy, or may be deposited in areas where stream energy is reduced (Coulthard and Macklin, 2003; Graf, 1996).

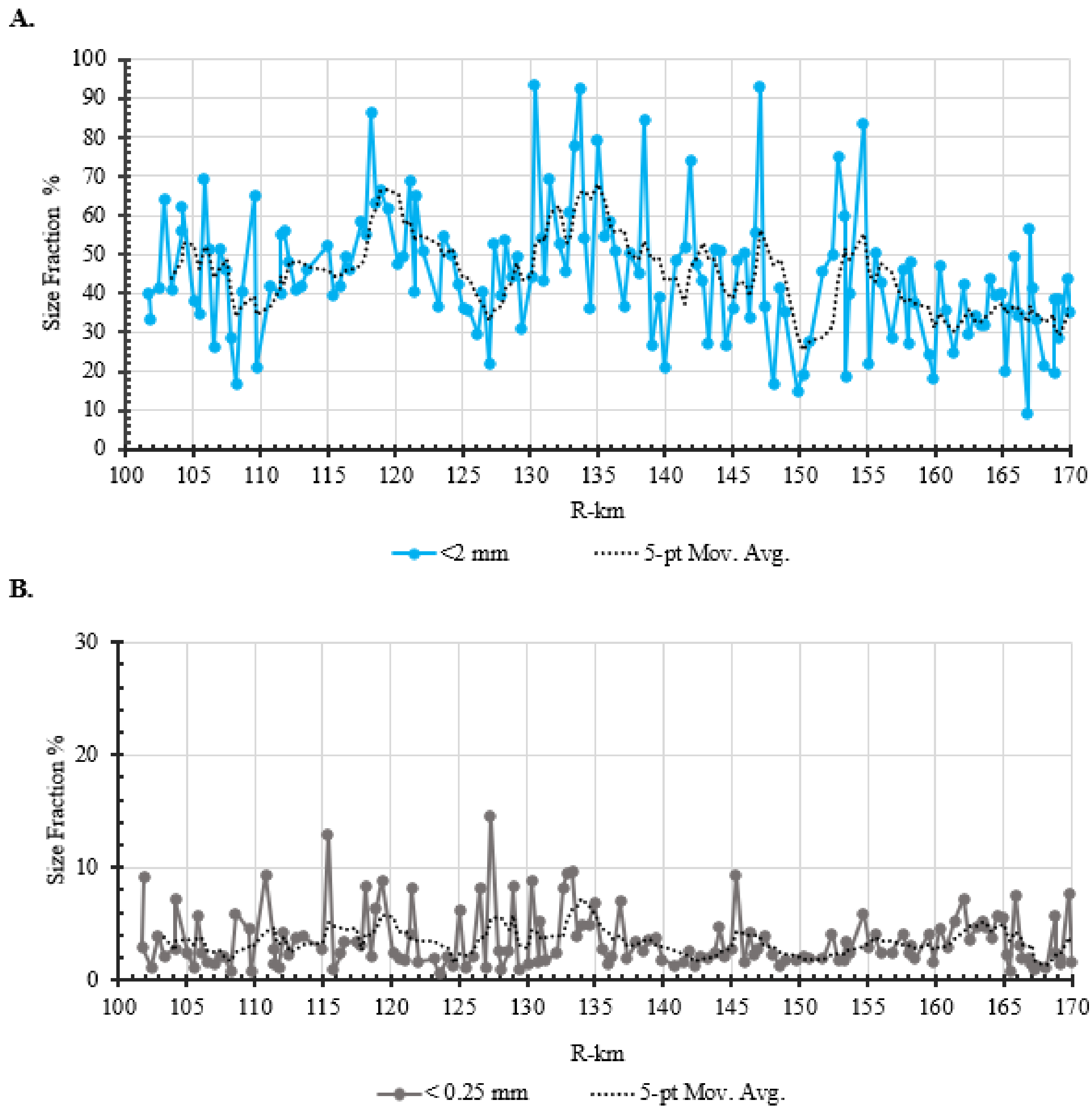


Figure 21: Downstream size trends in gravel bar bulk percentages for fine sediments. **A.** <2 mm. **B.** <0.25 mm.

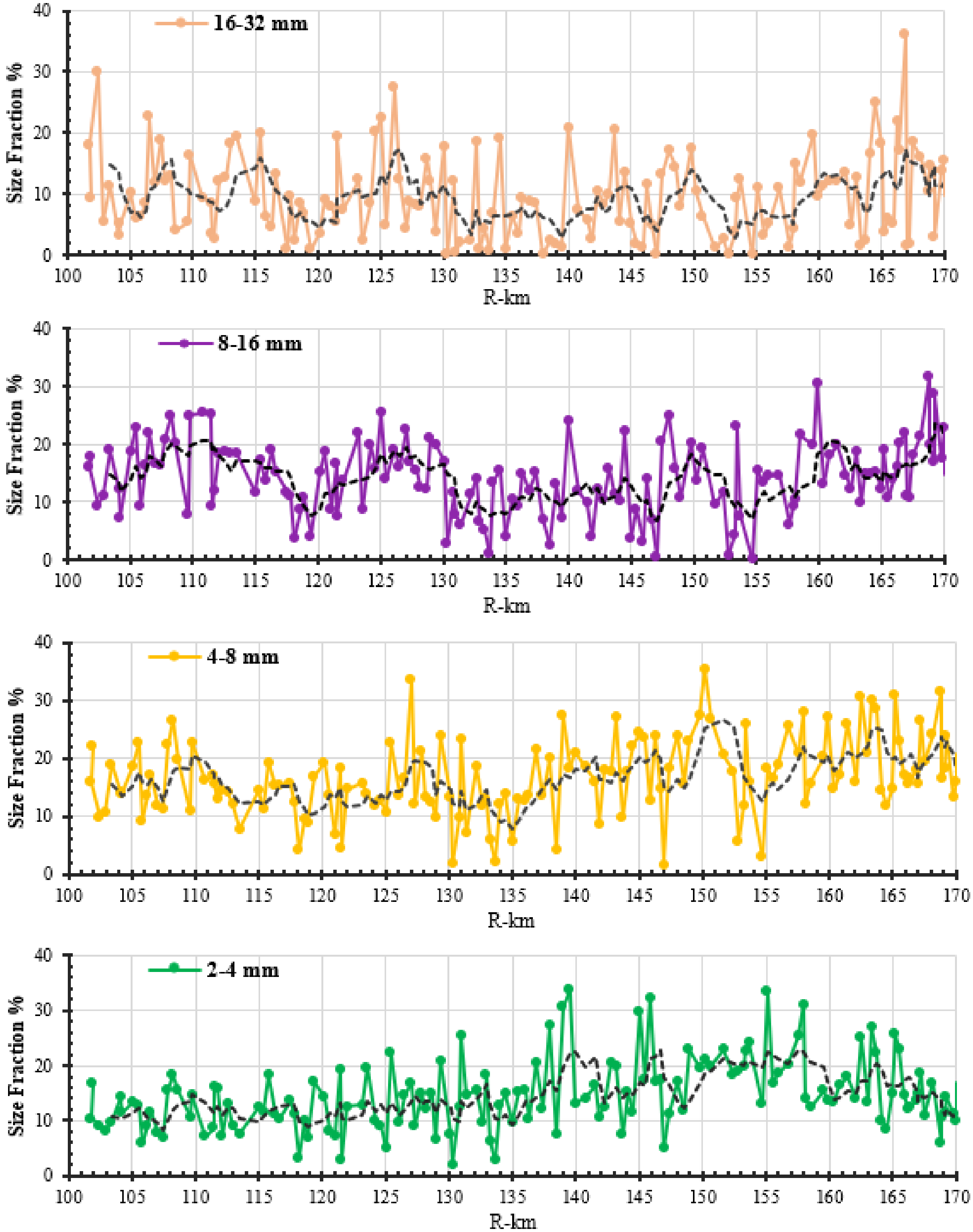


Figure 22: Sediment bulk percentages for 2-32 mm size fractions in gravel bar deposits. Dotted line represents 5-point moving average.

Similar to these results, MDNR (2010) and Pavlowsky et al., (2010) found the overall <32 mm bulk composition in bar deposits below Desloge was mainly dominated by sediments <2 mm in diameter. Pavlowsky et al., (2010) reported the bulk percentage of fine bar sediment (<2 mm) in control sites upstream from Leadwood (R-km 170.7) averaged around 20-35%. The <2 mm percentage below Leadwood ranged from 20-40% in bar sediments. They suggested the increase in sand-sized sediments may be due to tailings releases. Supporting this finding, Smith and Schumacher (1993) found coarse samples from the Desloge waste pile contained around 82% sand-sized sediments (0.63-2 mm). The increased bar presence of sand-sized sediments near Desloge likely resulted from the tailings release from the Desloge site in 1977.

Dolomite Sediment Percentages

As mentioned previously, the presence of mine waste in Big River channel deposits is indicated by the percentage of dolomite in gravel bar sediments <32 mm in diameter. Milling and beneficiation processes rarely produced wastes exceeding 16 mm (Pavlowsky et al., 2017) and almost no dolomitic sediments were found in the 16-32 mm size fraction. As such, for this study, determination of dolomitic percentages for bar sediments was confined to sediments <16 mm in diameter. As described in the Methods section, dolomite percentages were determined from lithology counts for the coarse-sized fractions (2-16 mm). In the very-fine fraction, the presence of dolomite was detected by elevated Ca levels. Dolomite percent was determined by subtracting background Ca levels from XRF Ca readings and then dividing by 217,000 mg/kg, the pure Ca content of dolomite. Initial XRF analysis of the very-fine size fractions (<2 mm and <0.25 mm) showed elevated Ca concentrations between Leadwood to Washington State Park between 15,000 to 157,000 mg/kg (Fig. 23).

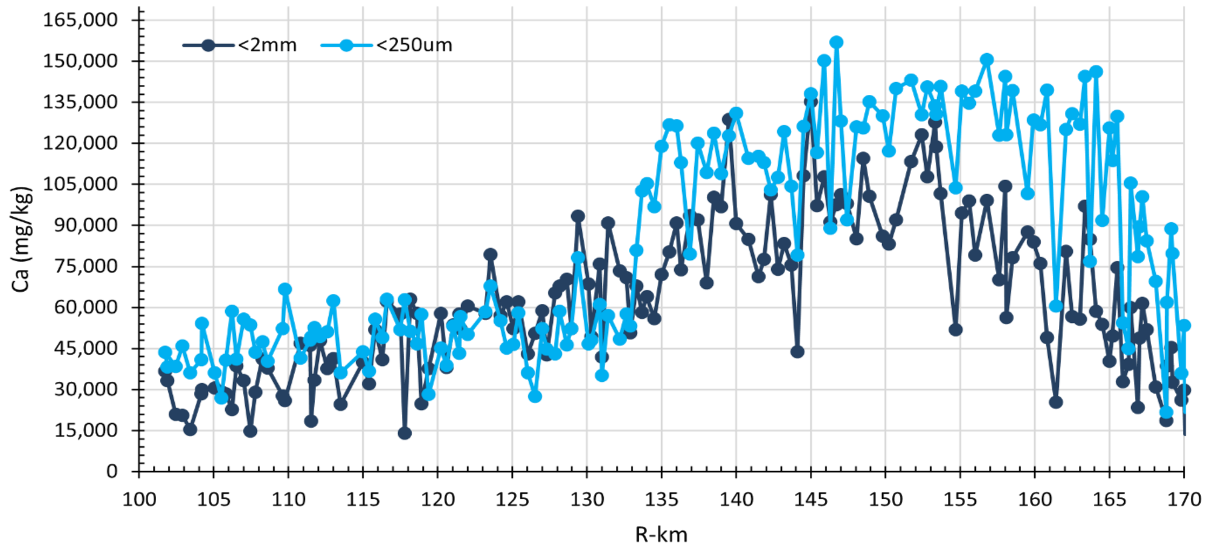


Figure 23: Measured Ca in fine (<2 mm) and very-fine (<0.25 mm) Big River bar sediments. Readings were adjusted using Aqua Regia values as described in Methods section.

In all size fractions, general dolomite percentage trends by river segment rose sharply below mine input sites and declined downstream (Table 4). The highest average dolomite percentages in all measured size fractions occurred in the reach between Flat River Creek (R-km 155) and the Cabanna Course tributary (R-km 132.5), similar to the patterns reported by Pavlowsky et al., (2010). Variations in dolomite concentration percentages, as indicated by CV%, were relatively high for all sizes.

Concentration peaks occurred for each size fraction in the following locations: <2 mm between R-km 153-139, 2-4 mm from R-km 155-137, 4-8 mm from R-km 155-142 and 8-16 mm sediments from R-km 155-145 (Table 5). The dolomite peaks occurred closer to point sources for the coarser sediments (8-16 mm and 4-8 mm) and farther downstream for the smaller sediments (2-4 mm) reflecting selective transport as described by Graf (1996). While the very-fine sediments (<2 mm) appear to peak ahead of the coarser sediments, it is expected that,

instead of being deposited, most of the finest sediments would have remained suspended and continued downstream (Graf, 1996; Coulthard and Macklin, 2003).

Table 4: Coefficient of variance percentage and mean dolomite percent for Big River gravel bar samples by river segment.

			Tailings Contribution (%)				
Segment	**n**	**Value**	**8 – 16 mm**	**4 – 8 mm**	**2 – 4 mm**	**<2 mm**	**<0.25 mm**
1	38	Mean	3.9	28.4	38.2	26.5	45.1
171-155 R-km		CV%	94	51	50	43	38
2	21	Mean	7.9	39.4	52.8	43.7	57.5
155-144.5 R-km		CV%	88	37	25	22	13
3	26	Mean	5.0	33.1	52.7	35.4	45.6
144.5 - 132.5 R-km		CV%	93	38	22	21	24
4	36	Mean	0.0	4.3	11.5	23.8	21.4
132.5 - 115.5 R-km		CV%	0	107	83	29	22
5	29	Mean	0.2	0.4	0.5	12.9	19.5
115.5 - 102.1 R-km		CV%	220	222	135	32	21

Not surprisingly, the calculated dolomite content in the <2 mm size fraction dominated the dolomitic sediment percentages below mining sites. While most of the 2-16 mm-sized dolomite percentages dropped below 5% just prior to Mill Creek (R-km 115), the <2 mm fraction averaged around 13% tailings and the <0.25 mm averaged 20% from Mill Creek (R-km 115) all the way to Washington State Park (R-km 101). Due to sediment mixing and the influx of tailings from Flat River mine locations, it is difficult to discern the influence of Leadwood and Desloge tailings below Flat River Creek. However, Flat River Creek represents a significant input of mine tailings. Considering the distance between Flat River Creek (R-km 155) and Mill Creek (R-km 115), the point where 2-16 mm dolomite percentages drop below 5%, an estimate of the maximum transport distance of legacy sediments from Flat River Creek is about 40 km. The use

of the Flat River tailings piles for waste disposal began in the early 1890s (Karsch, 1973). Therefore, the longest period of time that the coarse tailings were being released to the Big River would be about 120 years. The farthest downstream extent of the presence of tailings in the river represents the farthest transport of these legacy sediments, thus, an estimate of the maximum transport rate from the 1890s to 2014 would be around 330 meters per year. When estimated for each size fraction based on the point where the dolomite percentage reaches 0 consistently, the transport rates for each size fraction are 350 m/yr for 2-4 mm, 316 m/yr for 4-8 mm, and 175 m/yr for 8-16 mm (Table 5).

Table 5: Peaks in 2-16 mm dolomite percentages by size fraction and river kilometer (R-km).

Size Fraction	**Peak (R-km)**	**Downstream Limit (R-km)**	**Max Transport Rate (m/yr)**
2-4 mm	156	113	350
4-8 mm	156	117	316
8-16 mm	153	134	175

The calculated <2 mm and <0.25 mm dolomite percentages generally match the coarser sediment trends with a few deviations (Figs. 24 and 25). Trends rose steadily from Leadwood to Desloge, varied significantly by bar location, and maintained a significant presence throughout the entire study area. It is possible dolomite percentages may have been influenced by natural bar sediment distribution, where bar deposits tend to decrease in size from head to tail (Rosgen, 1996 in Owen et al., 2012), however, Pavlowsky et al. (2017) found relatively low variation between tailings percentages in Big River bar locations and bed and bar deposits. From the sample bar location just below Hwy K (R-km 146.7), the <0.25 mm fraction dolomite percentage rose to

peak at nearly 71% while the overall <2 mm dolomite content dropped to 43%. This location may have been affected by the release of very-fine sediments due to transportation along the highway, which supports traffic from the Bonneterre tailings site (Fig. 26). Both the <2 and <0.25 mm fractions also showed a pronounced increase at R-km 145 and the <2 mm fraction peaks at nearly 65% at this point. Located just above Terre Bleue Creek (R-km 144.5) and about 10 km downstream from Flat River, this site may reflect long-distance in-channel transport of a slug of sediments from the Flat River mine waste sites (Fig. 27). Sharp drops in both the <2 and <0.25 mm dolomite concentrations were observed just below the confluence with Terre Bleue Creek (R-km 144.5, locally called Pike Run), and again near Turkey Creek (R-km 136). This drop was also reflected in the overall bulk composition in these size fractions as well. Water depth near these confluences is relatively shallow and higher stream energy along with sediment dilution and mixing may be scouring the fine sediments and affecting the deposition at these locations. It may be interesting to explore the possibility of relationships between dolomite percentages, bar height, channel slope and water depth.

Dolomite concentration trends for the 2-16 mm size fractions showed similar increases and decreases at or very near the same bar locations. In the 2-4 mm size fraction, dolomite content peaked around 79% (the highest dolomite percentage for all size fractions) at the Flat River confluence (R-km 155) (Fig. 25). Average dolomite presence in this size fraction remained above 50% for over 35 km downstream, between the Flat River confluence and Bonne Terre (R-km 135) then steadily declined to zero toward Washington State Park (R-km 100). When represented geographically, the highest 2-4 mm dolomite percentages clearly occur between the Desloge tailings site and Bee Creek (Fig. 28).

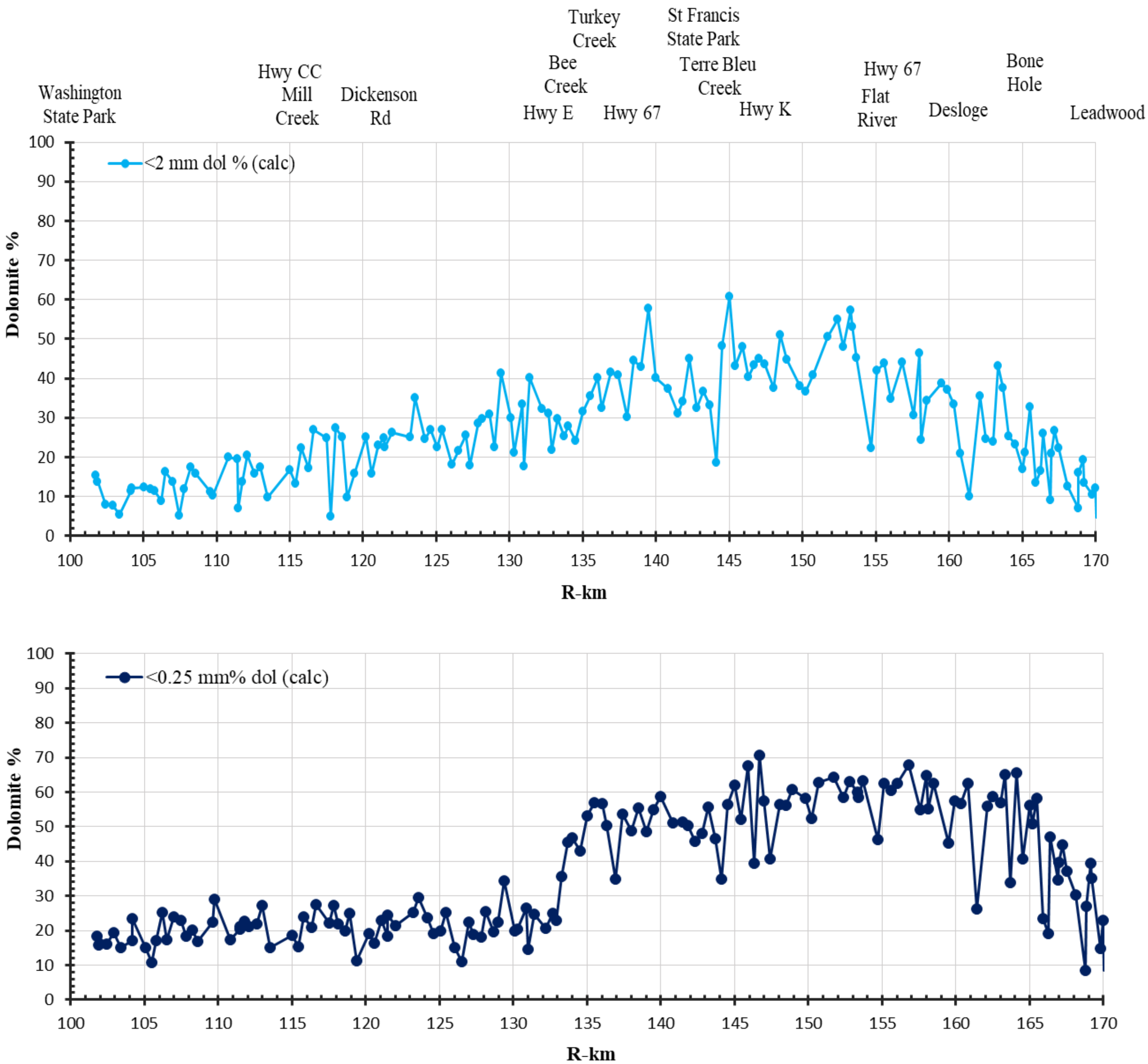


Figure 24: Distribution of <2 and <0.25 mm dolomite fragment percentages. Calculated from XRF Ca readings.

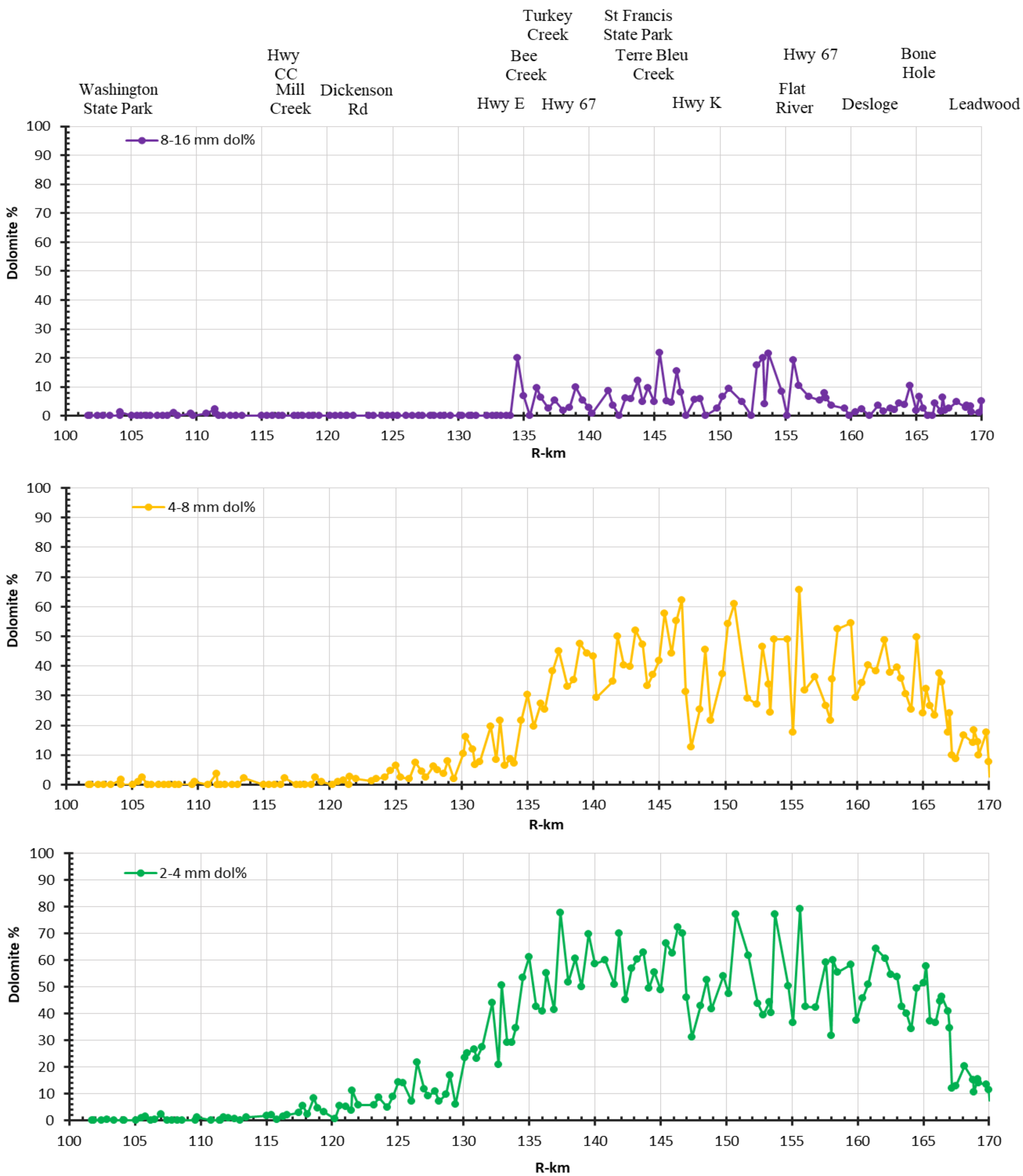


Figure 25: Distribution of 2-16 mm dolomite fragment percentages.

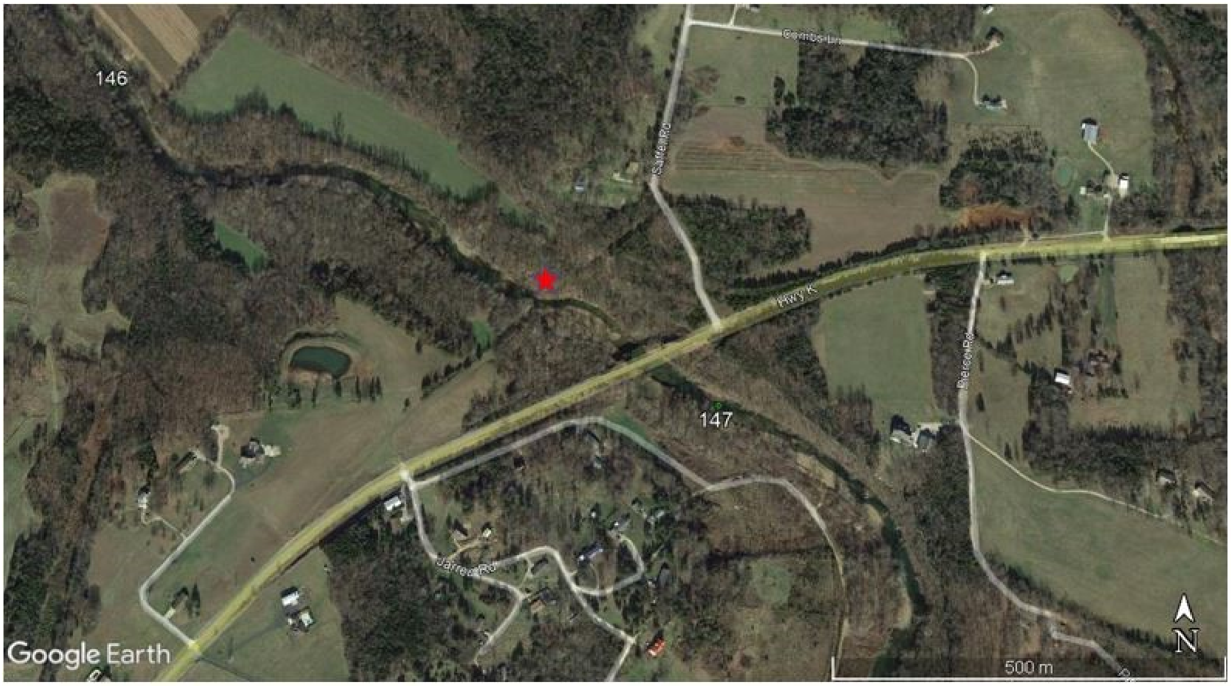


Figure 26: Google Earth image near Hwy K. Imagery Date: November, 2014. The gravel bar located at R-km 146.7 is starred just downstream from the Hwy K bridge.

Figure 27: Historical aerial image near Terre Bleue Creek. Image date: Nov. 2014. Terre Bleue Creek (R-km 144.5) is marked with a green star. The gravel bar location at R-km 145 is marked with a red star.

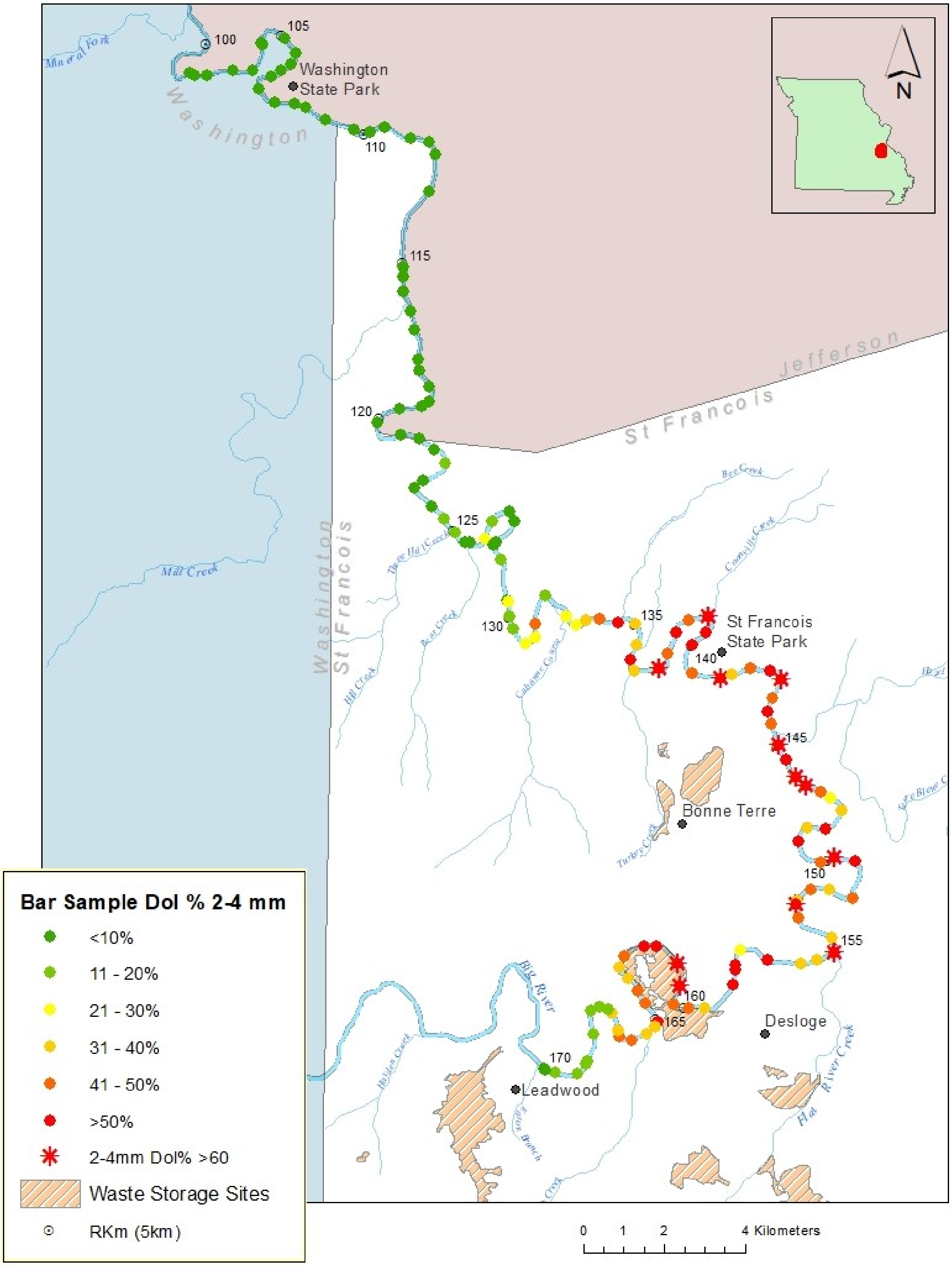


Figure 28: Geographic distribution of 2-4 mm dolomite percentages in Big River bar sediments.

The 4-8 mm dolomite percentages shared similarities with the 2-4 mm trends (Fig 25 above). Dolomite presence in this size fraction rose to near 50% just below the Bone Hole. Mine sediments at this location would have entered the Big River upstream at Eaton Creek (R-km 171), which drains the Leadwood tailings site. Dolomite concentrations in this area were likely influenced by the 2012 borrow pit dredging project, where sediments were excavated from the Bone Hole (R-km 165.3) and a downstream bar site (R-km 163.4) to evaluate the effectiveness of mine sediment removal as a remediation strategy on the river (Owen et al., 2012). The 4-8 mm dolomite percentages peaked at just over 62% at the Flat River confluence (R-km 155) and remained near or above 50% for at least 13 km downstream (R-km 142). Percentage trends gradually declined downstream, remaining above 40% through R-km 133, where very little to no dolomite in this size fraction was detected in bars below R-km 125. Geographically, most of the highest dolomite percentages in this size fraction occur below Flat River Creek (Fig 29).

Finally, dolomite percentages in the 8-16 mm size fraction remained around 10% below Leadwood and Desloge, then suddenly peaked near 22% at Flat River Creek (R-km 155) (Fig. 25), sugesting more sediments from this size fraction are probably coming from the Flat River waste piles. From the Flat River, the 8-16 mm dolomite percentages averaged around 7.4% with a few downstream locations bouncing close to 20% until just below Bee Creek, where 8-16 mm percentages dropped to less than 2% for the remainder of the study area (Fig. 25). The geographic distribution of this size fraction shows the majority of 8-16 mm sediments remain deposited within 20 kilometers of major input sources, consistent with sediment distribution patterns described by Graf (1996) (Fig. 30). Deposition patterns are likely being affected by variations in stream energy and geomorphology, activities outside the river, or possibly density differences due to residual sulfides in the sediments (Miller and Orbock-Miller, 2007).

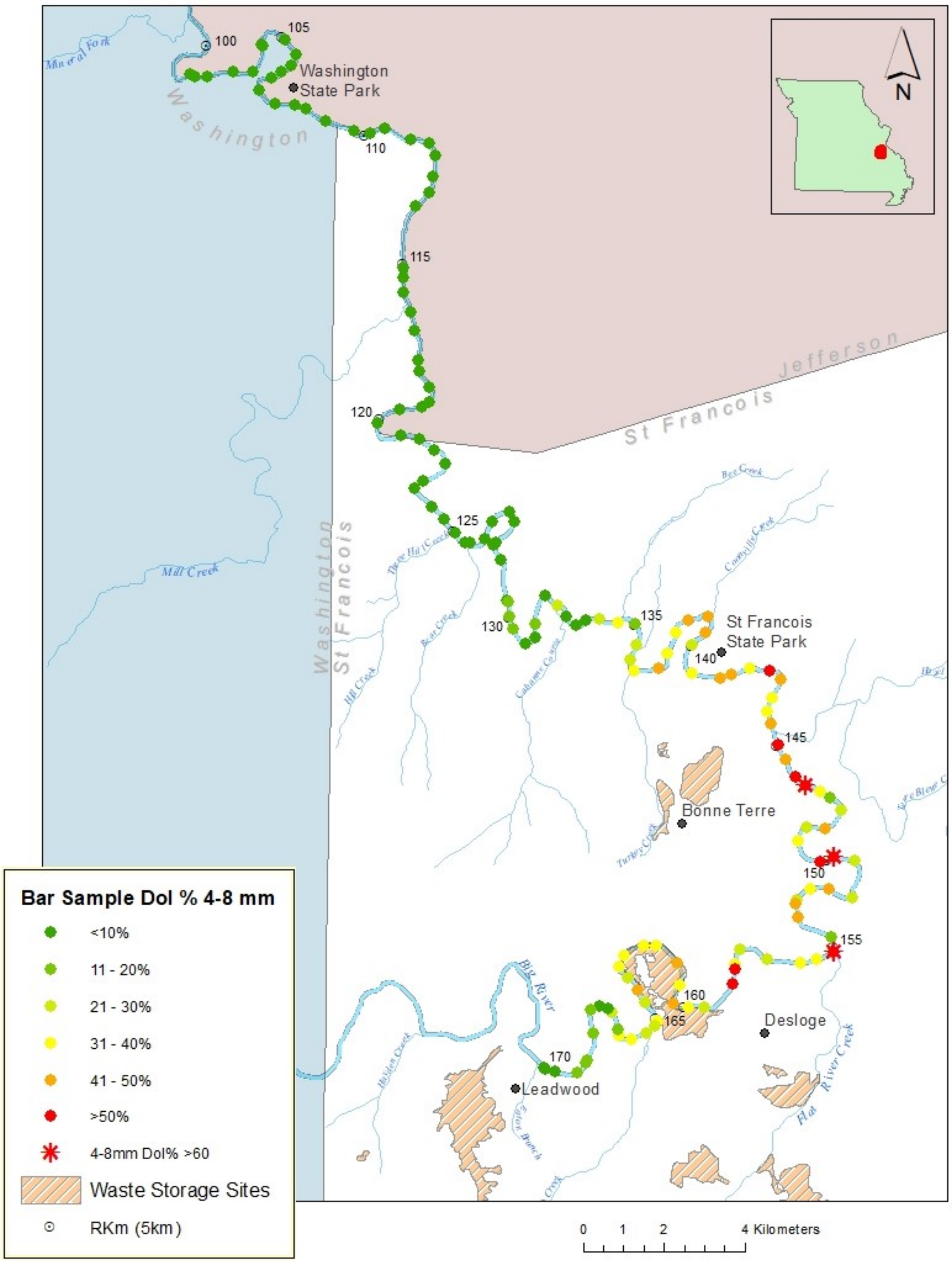


Figure 29: Geographic distribution of 4-8 mm dolomite presence in Big River bar sediments.

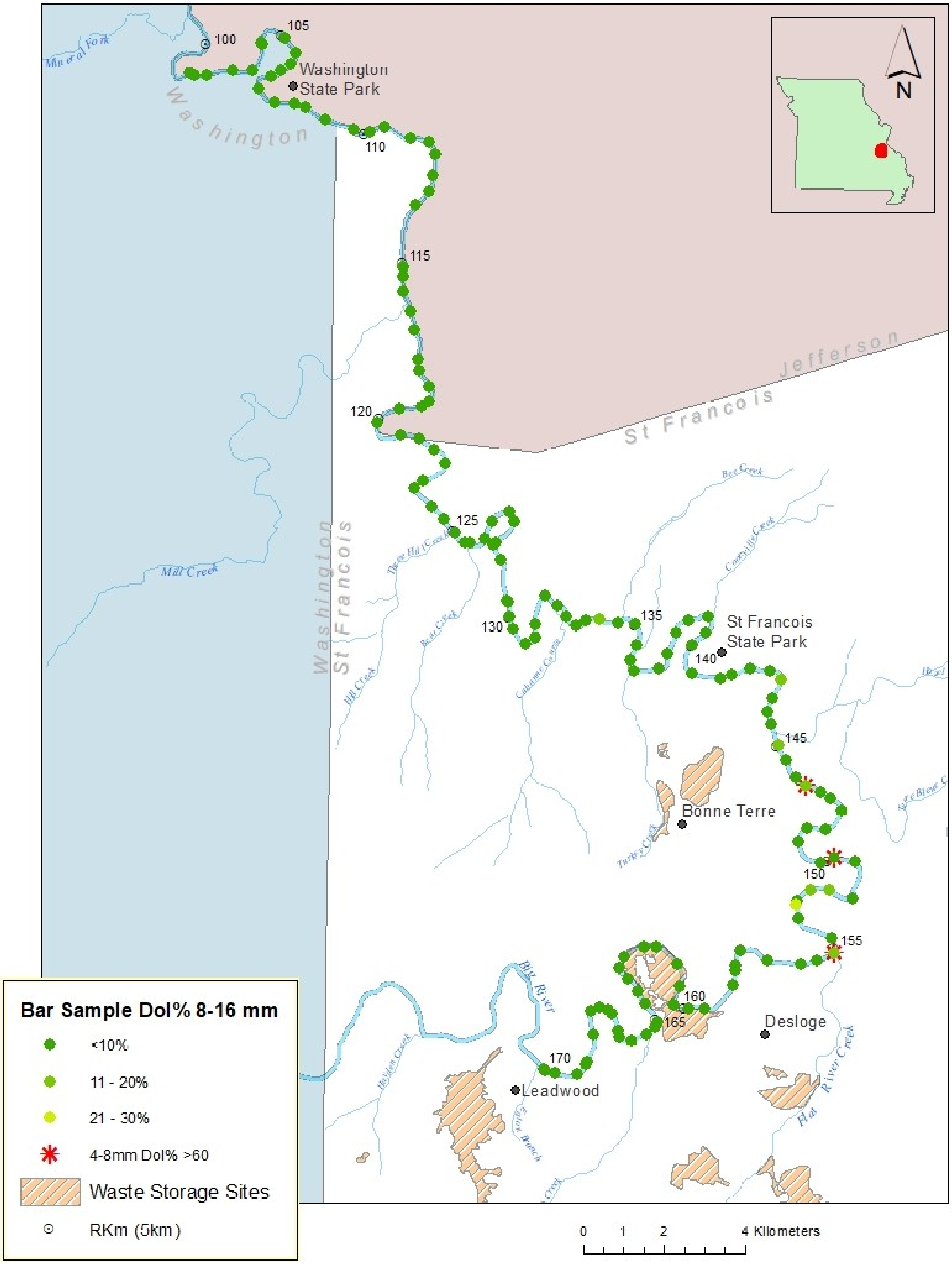


Figure 30: Geographic distribution of 8-16 mm dolomite percentages in Big River bar sediments.

Metal Concentrations

Previous studies approximated the background or natural levels for Pb and Zn before mining influence in the Big River by sampling sediments above the mine-contaminated reaches at 20 mg/kg and 34 mg/kg respectively (Pavlowsky et al., 2017). The guidelines established by MacDonald et al. (2000), used in both this and previous studies, sets the PEC limit for Pb at 128 mg/kg and 459 mg/kg for Zn. As expected, the PEC limit for Pb is exceeded throughout the mine-affected study area in both the fine and very-fine size fractions (<2 mm and <0.25 mm, respectively) by 1 to over 50 times the PEC limit (Fig. 31). Further, in both size fractions, Pb concentrations increase sharply, then steadily decline away from mine waste sources. Geographic mapping clearly shows the entire study area remains above 3x the PEC limit for the <2 mm fraction and the <0.25 mm fraction remains above 10x the PEC limit from R-km 170 through around 134 (Figs. 32 and 33).

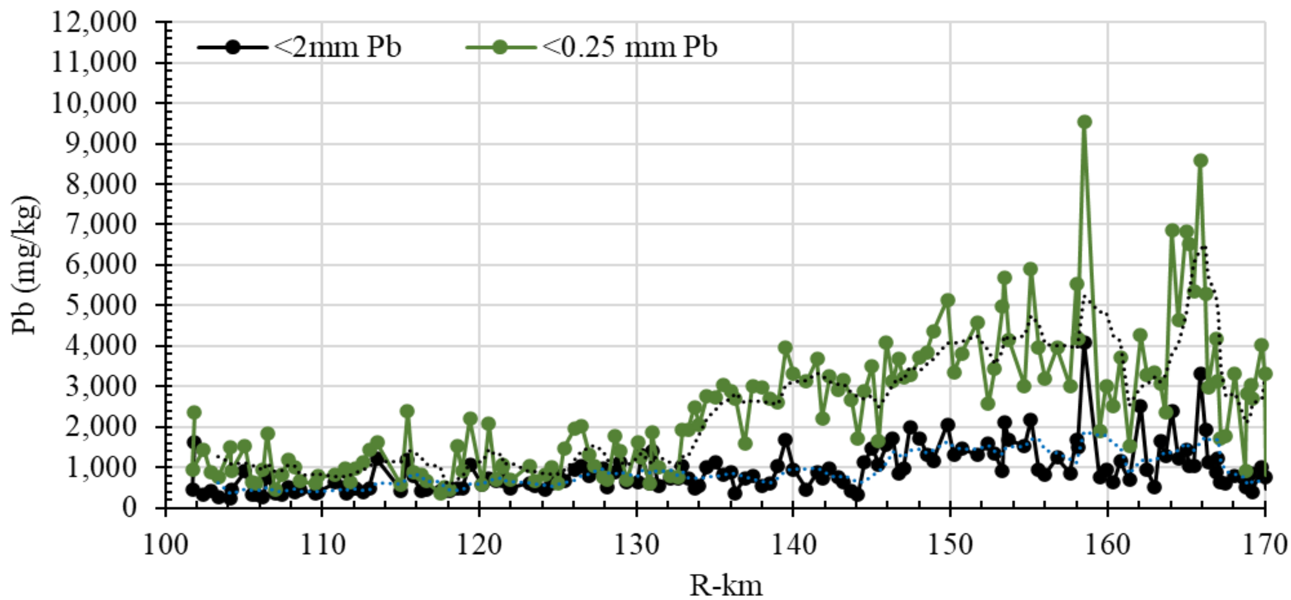


Figure 31: Pb in <2 and <0.25 mm Big River bar sediments. Moving average (5-pt) is shown as dotted line. PEC limit for Pb is 128 mg/kg.

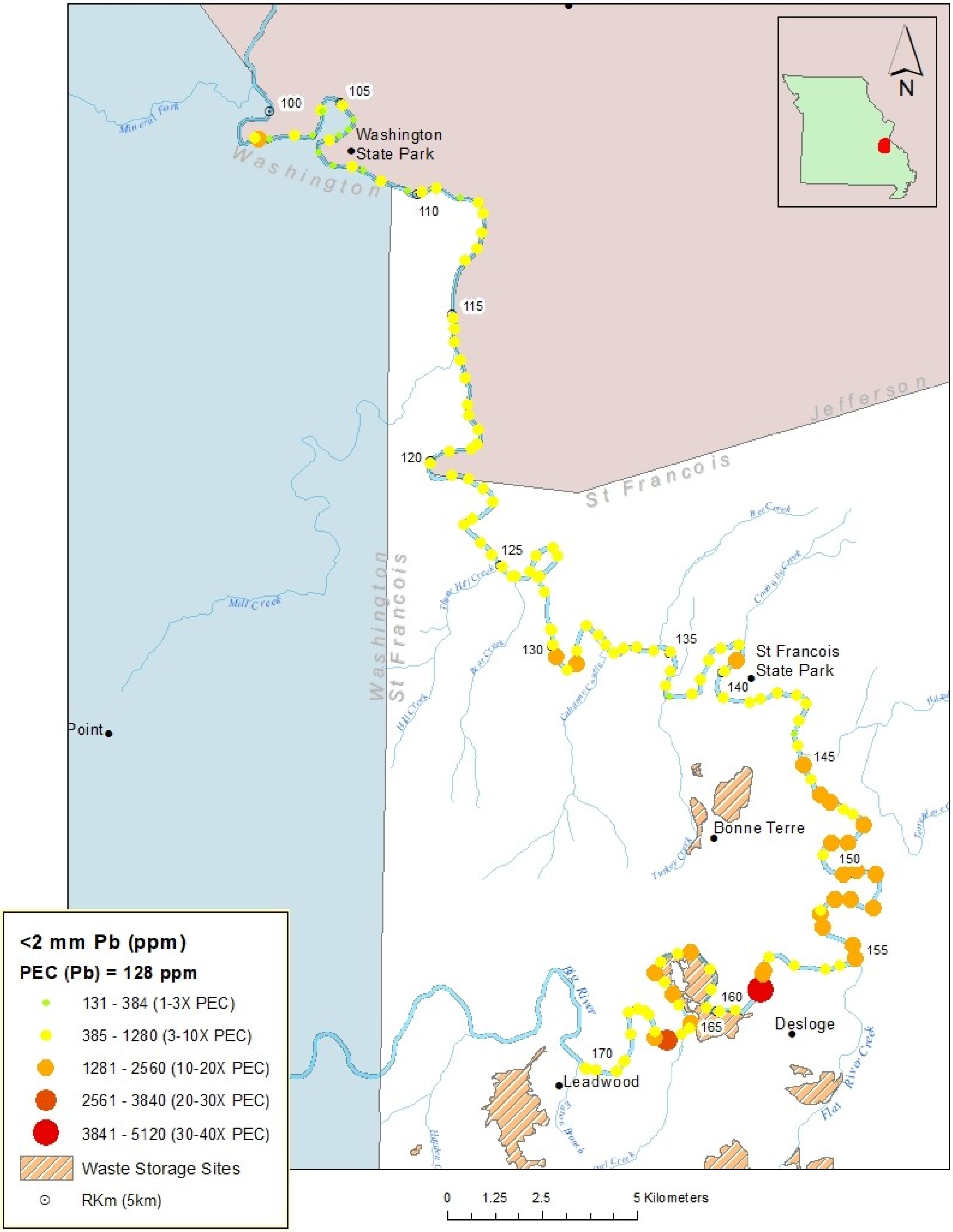


Figure 32: Geographic distribution of Pb contamination in <2 mm Big River bar sediments.

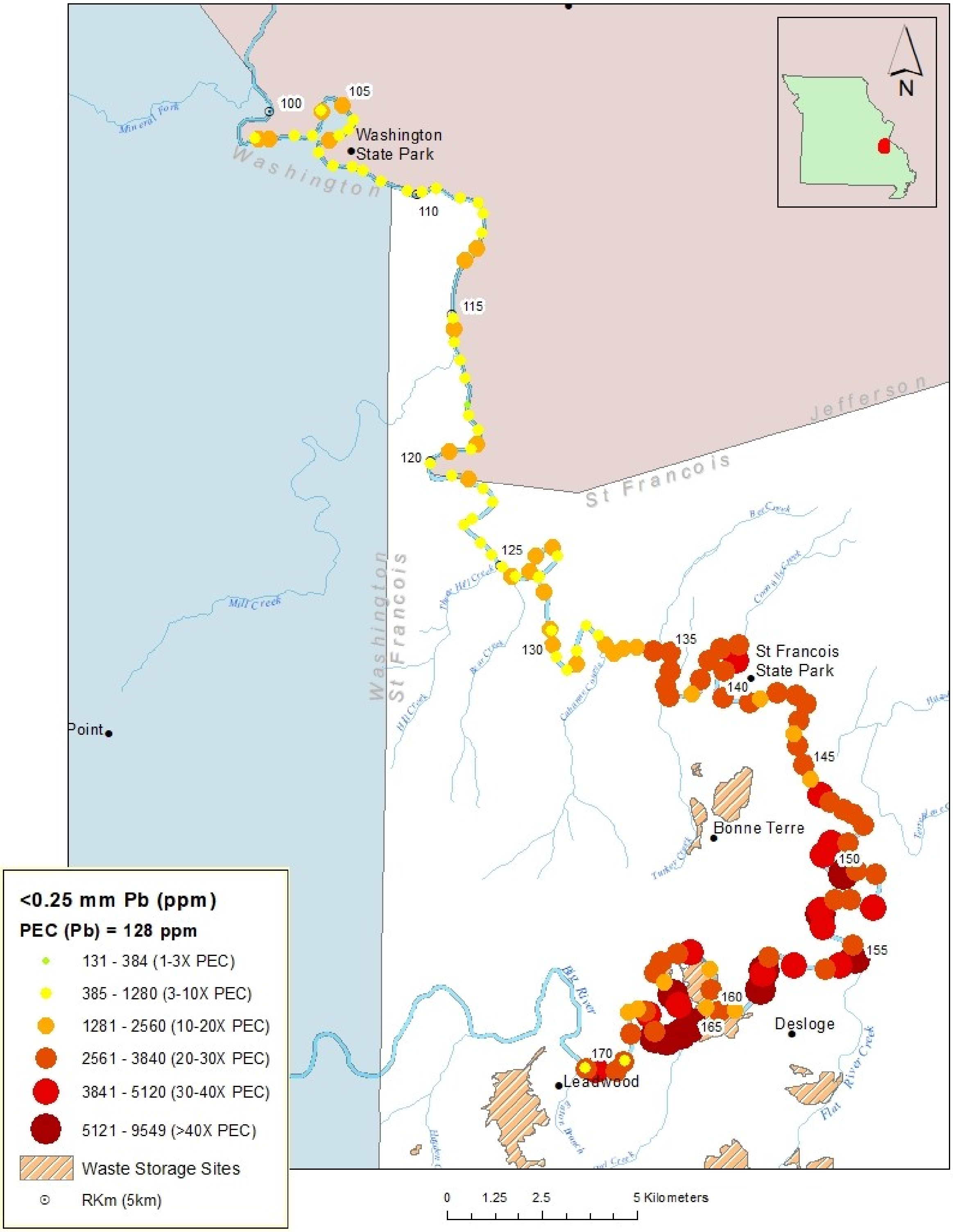
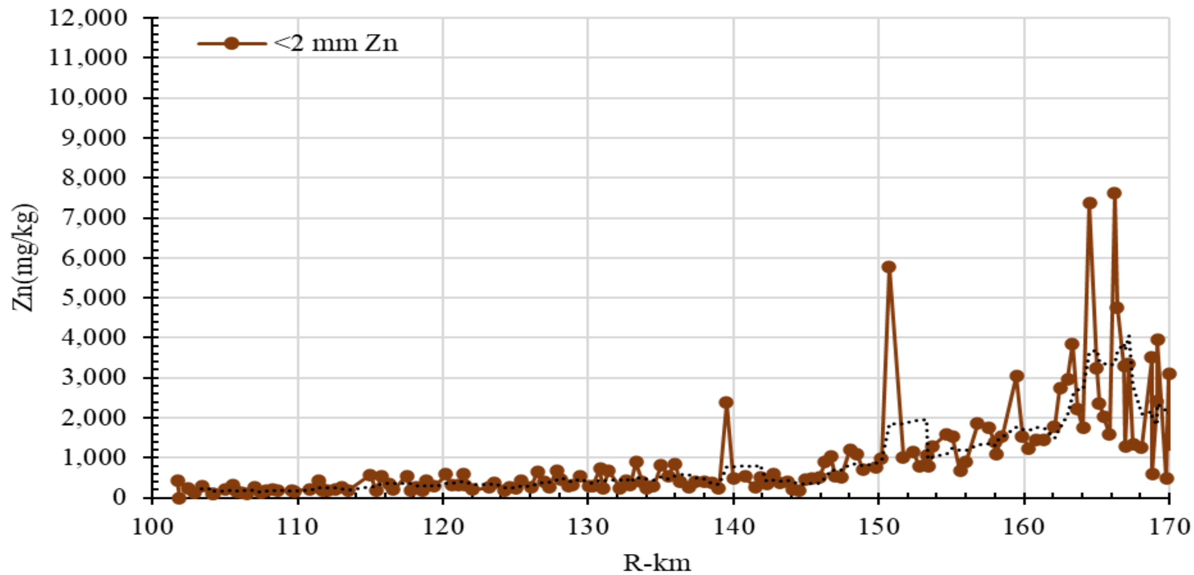


Figure 33: Geographic distribution of Pb concentrations in very-fine bar sediments (<0.25 mm).

The highest Pb levels for both the <2 mm (4,100 mg/kg; 32 times PEC limit) and <0.25 mm sediments (9,550 mg/kg; almost 75 times PEC limit) were detected at R-km 158.5, a very large, constricting, side bar below the Desloge pile. As mentioned previously, in 1977, around 38,000 m^3 of tailings slumped into the river from the Desloge pile (Newfields, 2007; USFWS, 2008). The bar is also located immediately downstream from a railroad bridge crossing which may contain residual contaminated ballast materials. Operating nearby are the Valley Minerals, LLC and Missouri Lime companies. It is possible that surface runoff, accumulation of air-borne particulates and transportation of materials across the bridge contributed to the very-fine Pb concentration here. The next highest Pb readings occurred in both fractions at R-km 165.9, just above the Bone Hole excavation site, where <2 mm Pb levels were just over 3,300 mg/kg (25xPEC) and <0.25 mm was almost 8,600 mg/kg (69xPEC). The remainder of the <2 mm Pb levels were less than 20 times the PEC (<2,560 mg/kg). However, in the <0.25 mm fraction very high levels (20-50xPEC) persisted between R-km 167 (about 3 km downstream from Leadwood) and R-km 153.5, just below the Flat River confluence.

Not surprisingly, measured Zn levels are generally highest in bar deposits above Flat River (R-km 155) with the highest measured Zn levels at close to 25 times the PEC levels: 11,435 mg/kg (R-km 164.10) and 10,391 mg/kg (R-km 165) (Fig 34). This is likely an expression of the unique geochemical signature of Leadwood and Desloge wastes which typically possess higher Zn concentrations due to local Zn enrichments in ore bodies at these mines (Pavlowsky et al., 2010) (Figs 37 and 38). This is especially prevalent in the <0.25 mm fraction. Due to their higher Zn content, waste sediments from these sites may pose a greater risk for release, dissolution, and adsorption of Zn as they weather. Zn levels in the <2 mm fraction dipped below the PEC about 10km downstream from the Flat River confluence, likely due to

sediment dilution. The <0.25 mm Zn levels remained above the PEC for the majority of the study site, but also begin to dip below the PEC threshold about 23km downstream from Flat River.



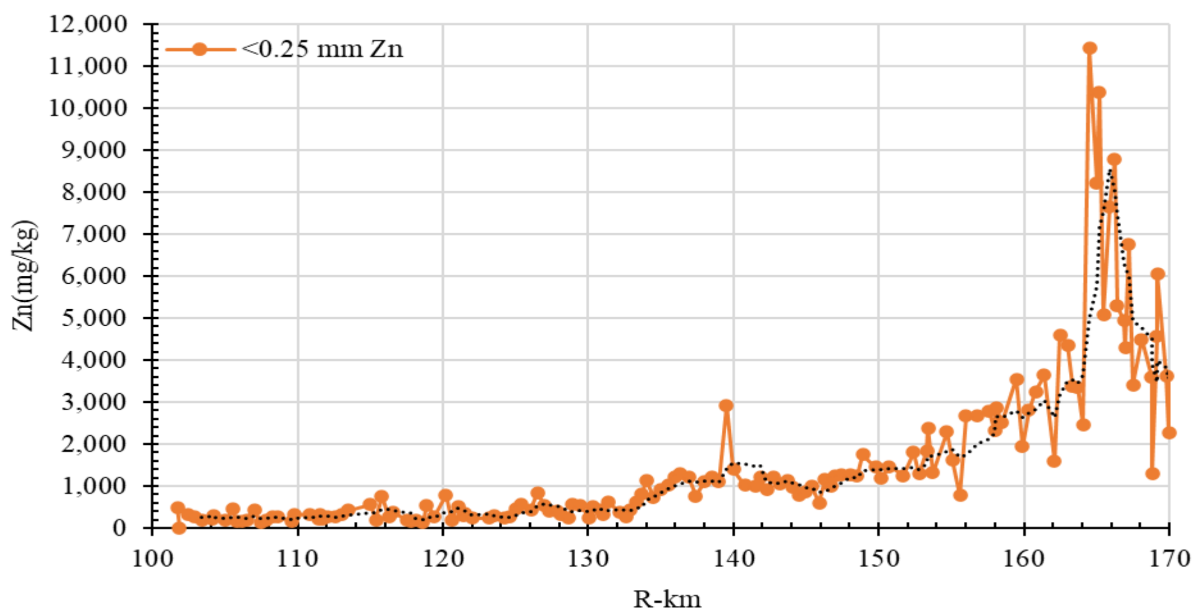


Figure 34: XRF measured Zn levels in <2 and <0.25 mm bar sediments. Dotted line represents five-point moving average. PEC limit for Zn is 459 mg/kg.

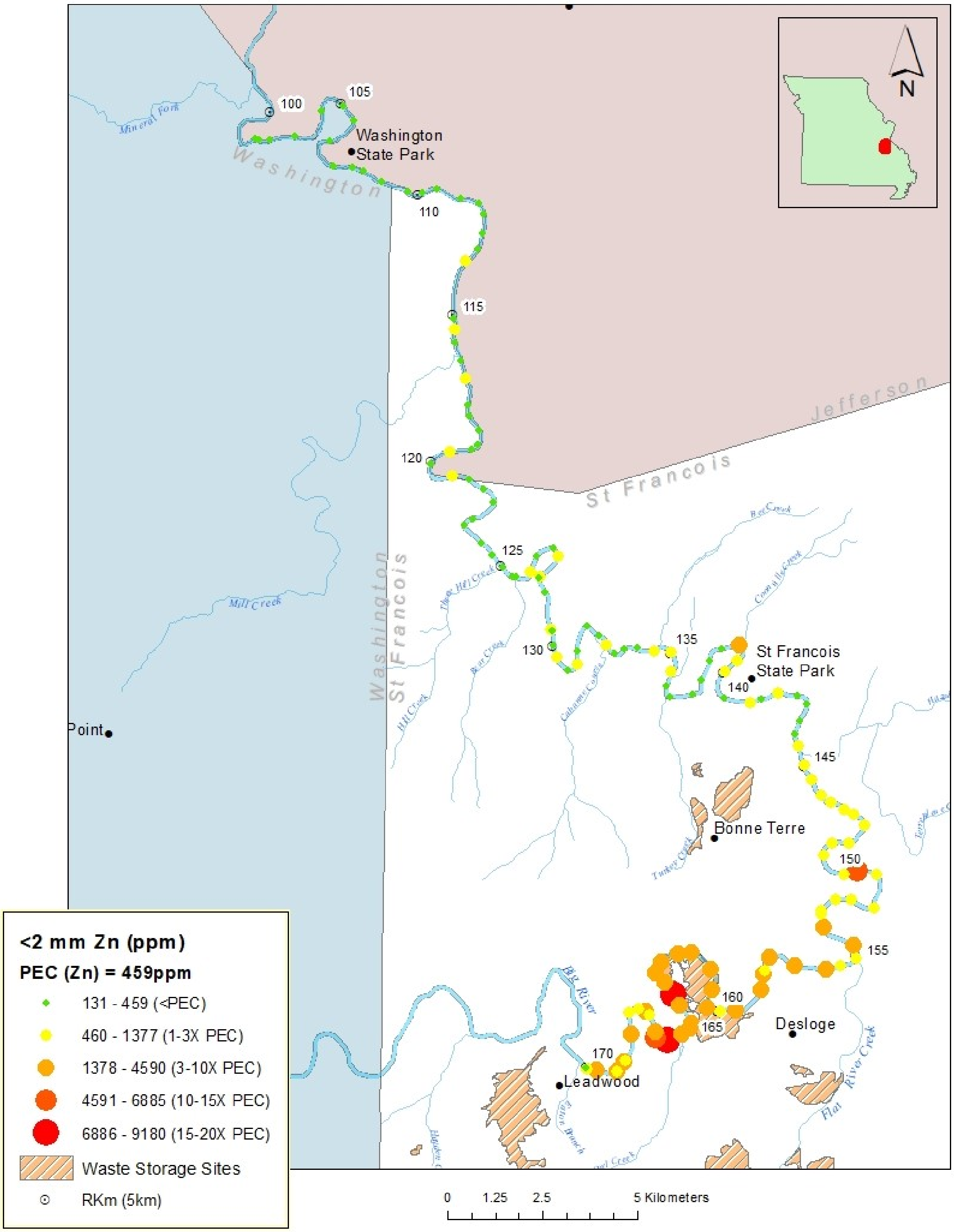


Figure 35: Geographic distribution of Zn levels in <2 mm bar sediments.

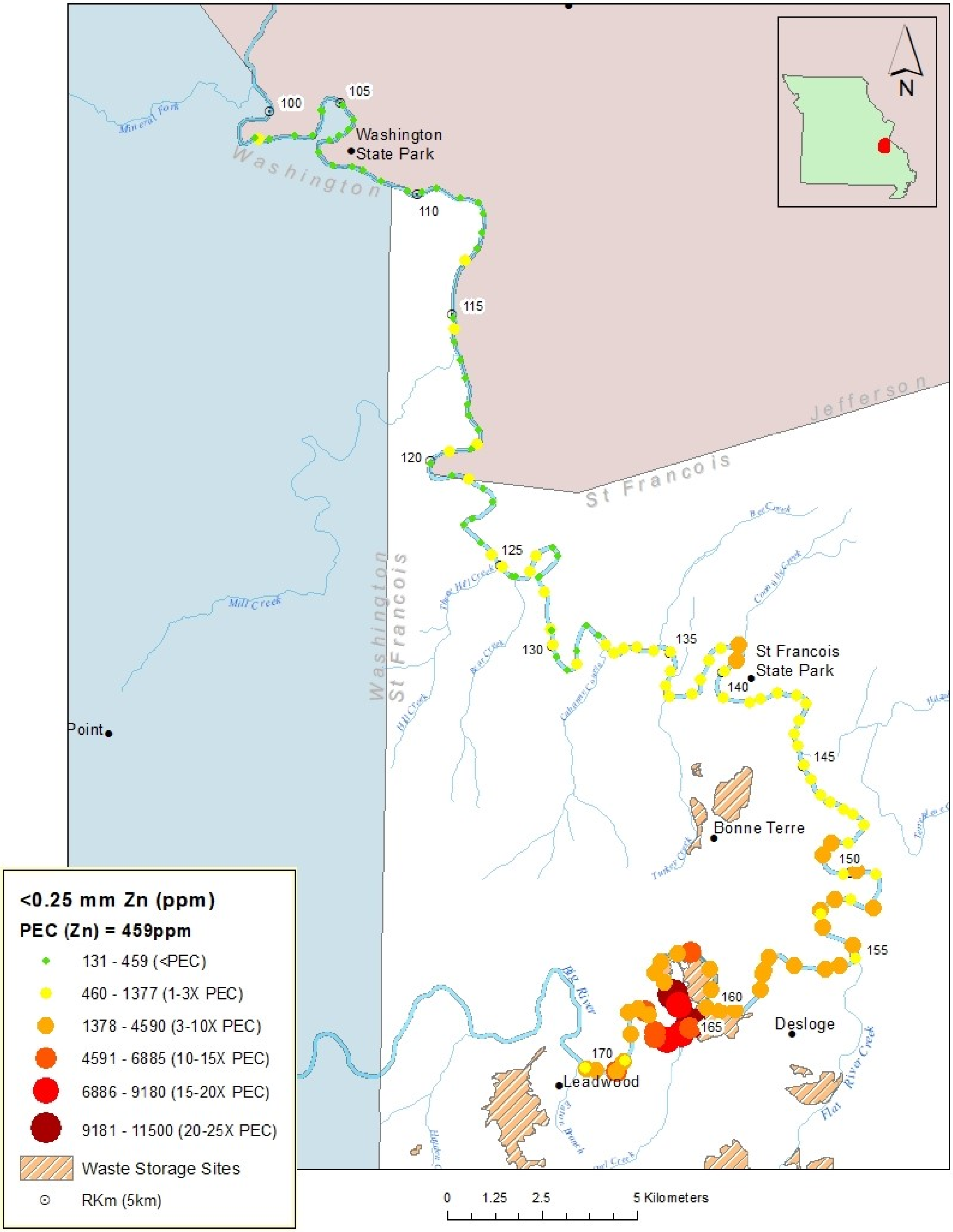


Figure 36: Geographic distribution of Zn levels in <0.25 mm bar sediments.

The ratio of Pb to Zn can be useful in determining the unique geochemical signature of ore bodies from different mines. As mentioned previously, local Zn enrichment produced differing levels of Zn concentrations. According to Pavlowsky et al. (2010), each mine site along the Big River exhibits a characteristic Pb/Zn ratio. As expected, the fine and very-fine Pb/Zn ratios trend upward downstream from Leadwood as source Pb levels rise and Zn levels decline (Fig. 39). Leadwood tailings have a characteristically high Zn content, and therefore the lowest Pb/Zn ratio, compared to other mine sources in the region. Mixing of sediments at Flat River makes it more difficult to determine accurate measurements for these ratios for use in rate of transport calculations. However, Zn levels below the Leadwood site are notably higher than any of the other sites. The Pb/Zn ratio for Leadwood sediments, therefore, is much lower than at other sites. It is assumed that mine waste entered the Big River from the confluence of Eaton Branch, which drains the Leadwood waste areas (R-km 171) (Fig. 37).

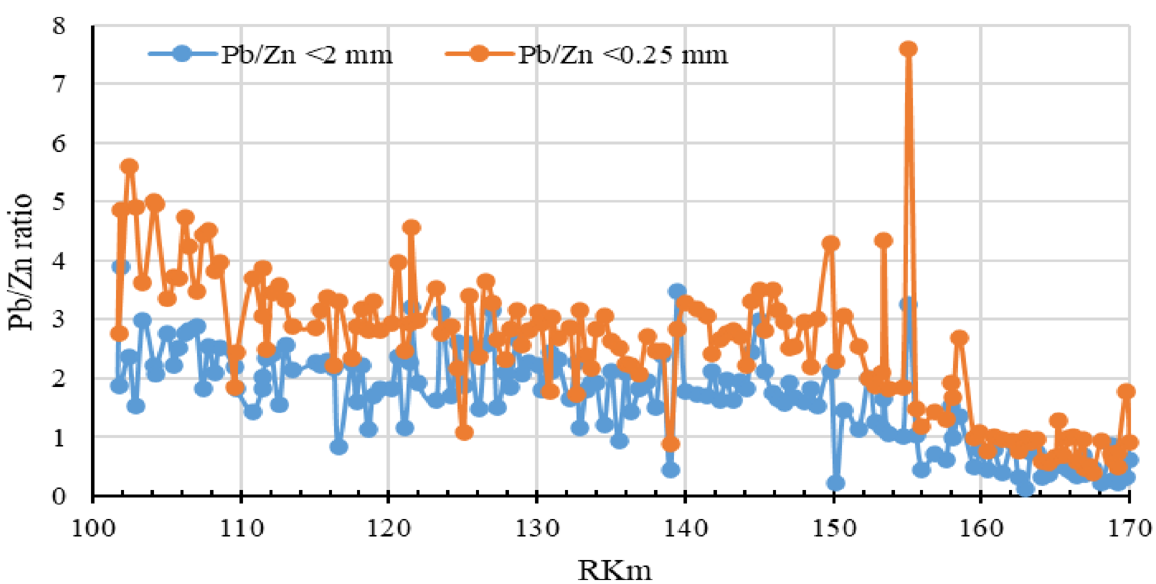
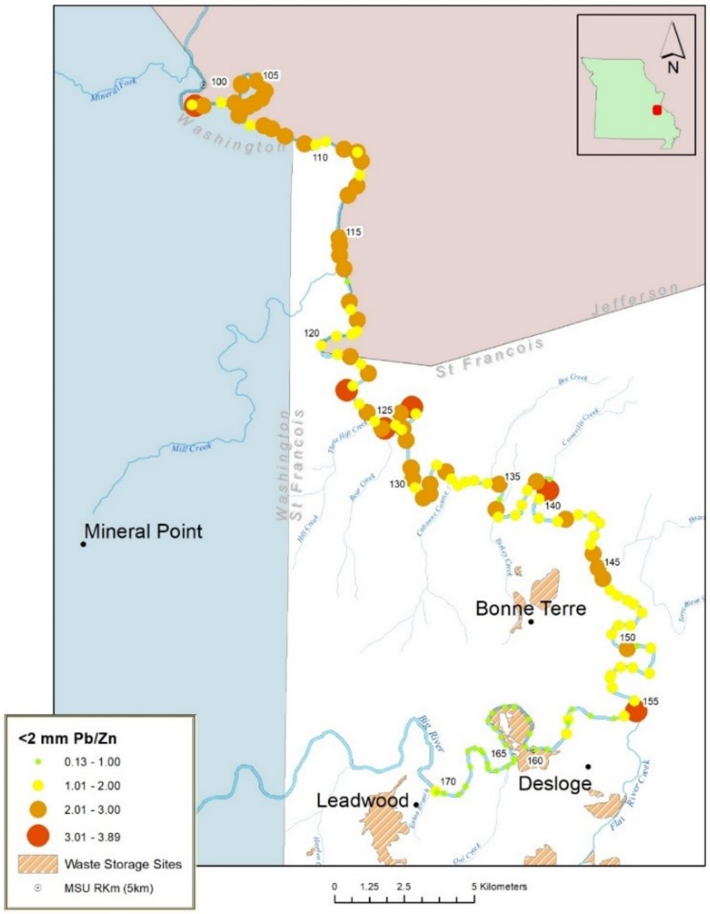
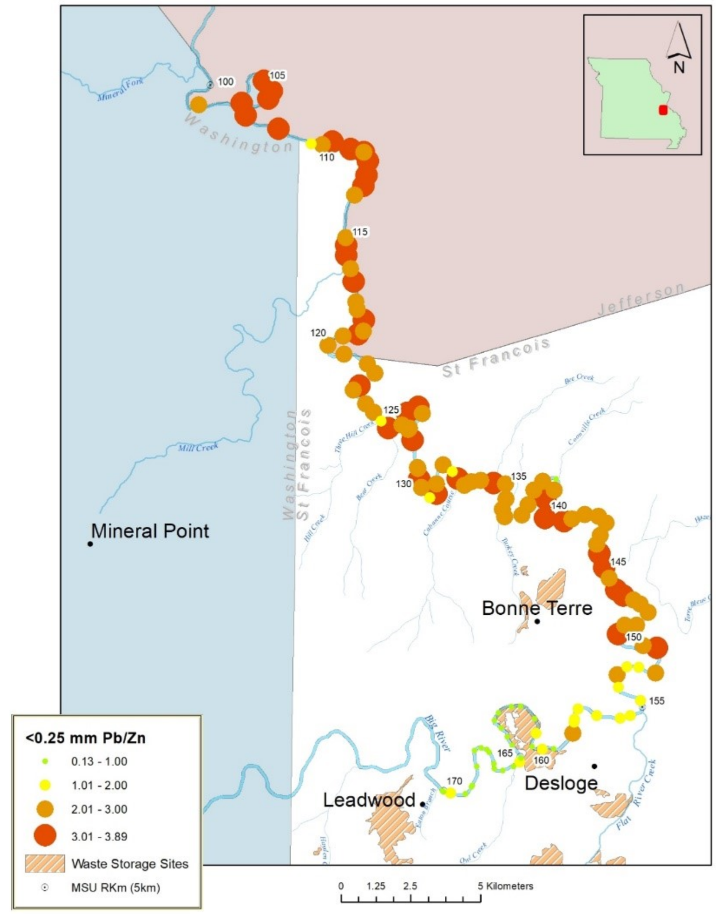


Figure 37: Pb/Zn ratios for both <0.25 mm and <2 mm size fractions.



A.



B.

Figure 38: Spatial distributions showing Pb/Zn ratios in bar sediments. **A**. <2 mm and **B.** <0.25 mm. High Pb/Zn ratios are characteristic of Flat river waste piles and reflect dilution of Leadwood and Desloge sediments.

Coarse Tailings Analysis

Petrographic Analysis. A small sample of coarse chat (4-8 mm) was obtained for this study from the Federal Mine-Mill complex, now known as the Missouri Mines State Historic Site in Park Hills, MO. The sample chat grains originated from the Federal above-ground chat pile near the mill, and, to the author's knowledge, were exposed to episodic weathering within the pile but remained outside the fluvial system. Thin section grain mounts were prepared from selected grains for petrographic analysis as described in the methods section.

Microscopic analysis of the Federal mill chat grains showed that after milling and beneficiation processes, the grains still contained a significant amount of residual sulfide crystals (Fig. 39, A-C). Photomicrographs revealed mainly subhedral carbonate grains, most <1 mm in diameter, along with finely disseminated sulfide crystals which appeared to concentrate along boundaries between the grains (Fig 40, A-C). Mineral grain boundaries may represent areas of weakness as the high-reactivity carbonates within the particles dissolve. Further, dissolution along these boundaries may both release sulfide crystals and allow clusters of sulfide-rich dolomite grains to become mechanically detached, increasing surface area for further weathering (Israeli and Emmanuel, 2018). As mentioned previously, Schmidt et al., (1987) suggested that sulfides in waste particles found in the Big River are continuously becoming more soluble through oxidation processes, making them more available to carbonate precipitation and binding to living and non-living organic matter. It is reasonable to assume that higher sulfide concentrations within the dolomitized clay boundaries of unweathered chat grains may present an increased risk for release, dissolution, adsorption to fine sediments within the fluvial system, or oxidation to a more bioavailable form when these chat particles are weathered, transported, and deposited within the fluvial system.

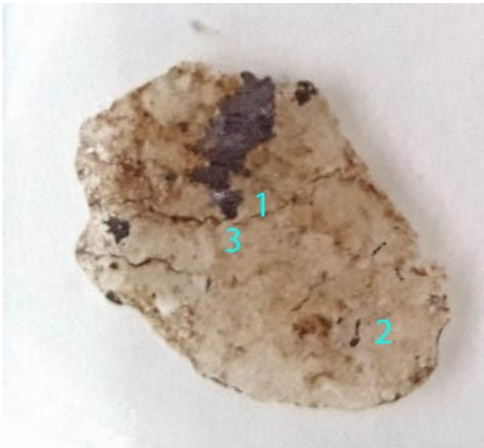


Figure 39A: Macroscopic view of prepared coarse chat dolomite grain thin section. Fed Grain 1-1 from Federal mines area. This grain measures 1.2 cm on long axis and 0.8 cm on short axis. Residual macroscopic galena crystals are visible. Regions are marked to correspond with following photomicrographs.

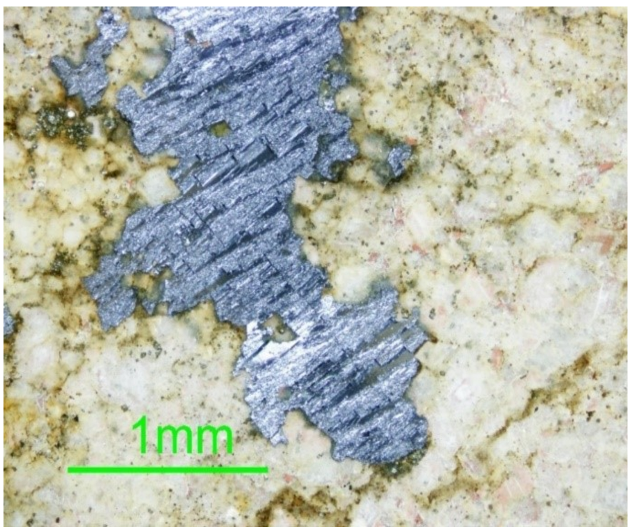


Figure 39B: Photomicrograph of middle and lower section of largest galena crystal from Fed Grain 1-1, Region 1. Reflected light, 5X, taken with a Nikon Eclipse LV100 POL.

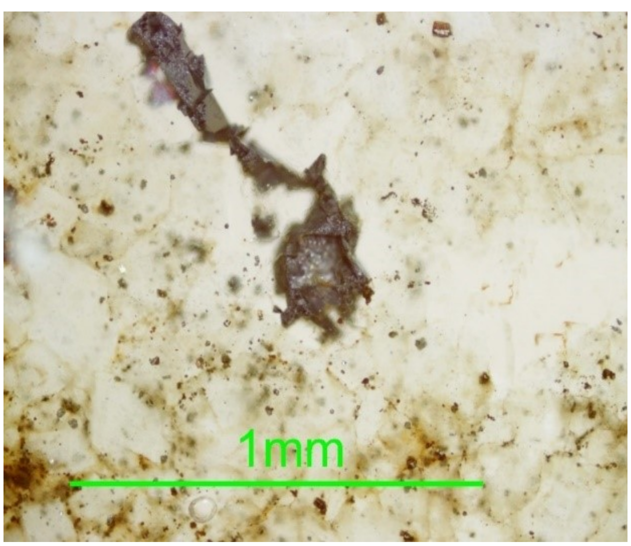
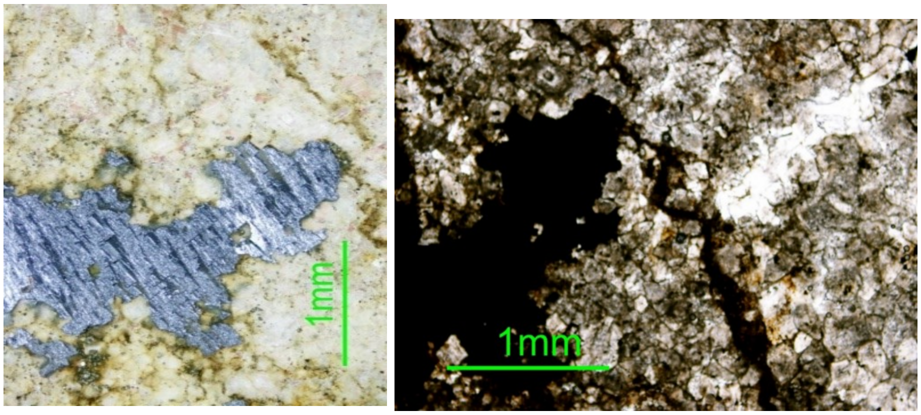
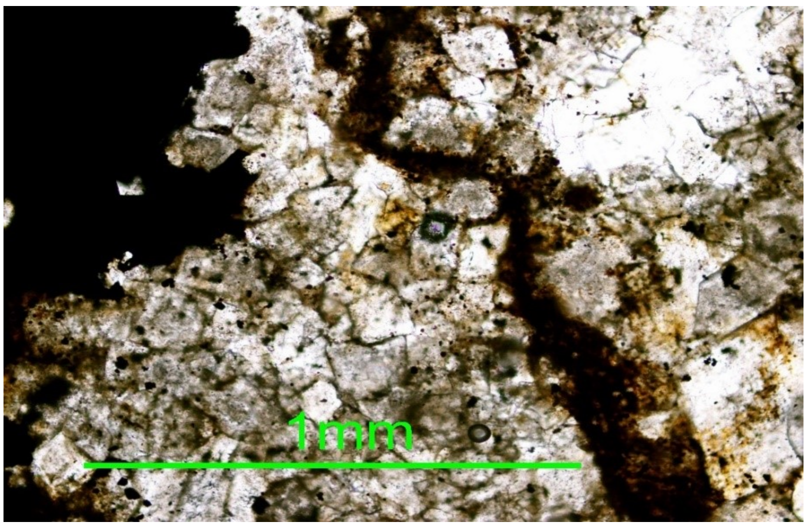


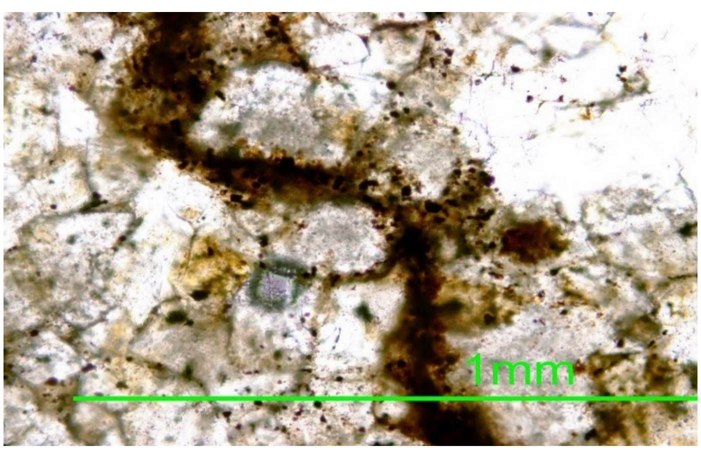
Figure 39C: Photomicrograph from Fed Grain 1-1, Region 2. Reflected light photomicrograph, 10X, showing macroscopic galena crystal from region 2. Finely disseminated microscopic galena, sphalerite, and pyrite crystals within and around the dolomite grains are visible.



A.



B.



C.

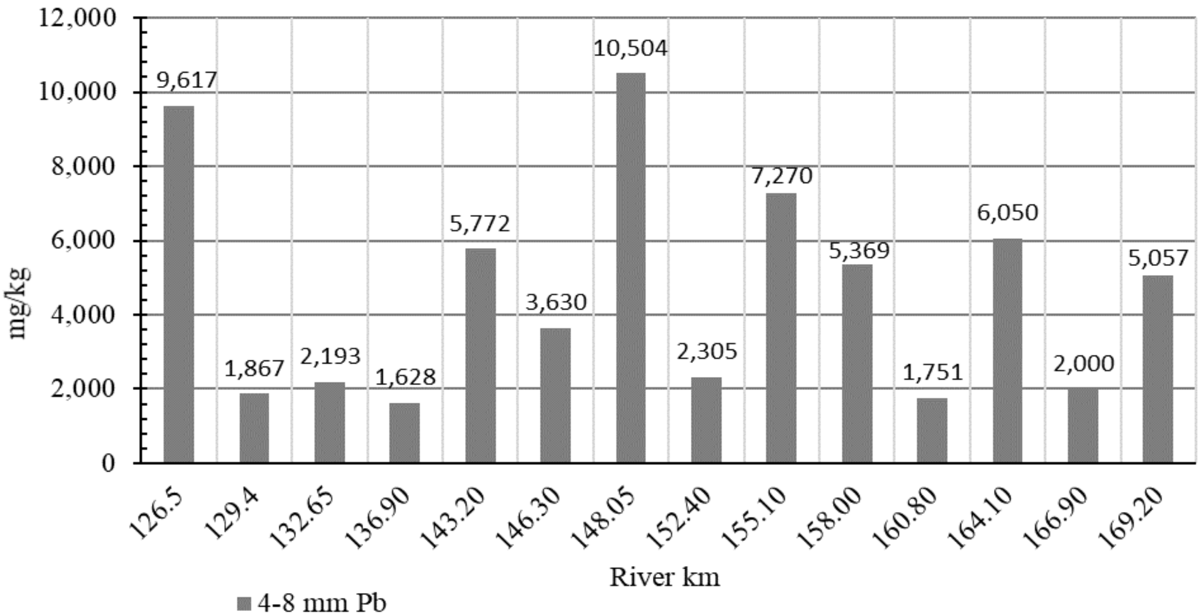
Figure 40: Photomicrographs from Fed Grain 1-1, Region 3 (refer to Fig 41). The subhedral (planar-S) carbonate matrix is visible in all three views. **A.** Rotated reflected-light view of large sulfide deposit from Region 3 alongside transmitted-light view of same region at 5X. **B. and C.** Transmitted-light microphotographs showing increasing magnifications of same view at 10x and 20x respectively. The dark/opaque regions in these transmitted-light views are sulfide minerals. Larger sulfide concentrations seem to occur near grain boundaries.

XRF Analysis. From collected bar samples, three subsamples of 8-16 mm, fourteen 4-8 mm, and seven 2-4 mm coarse dolomite chat grains, as well as three subsamples of 4-8 mm natural sediments were picked for XRF analysis to assess residual Pb and Zn composition of weathered chat grains. Farther downstream, sample selection was somewhat limited by scarcity of available dolomite grains within original samples. XRF analysis of weathered chat grains showed residual Pb content between 1,600 to 10,500 mg/kg for 4-8 mm chat, with an overall average of around 4,600 mg/kg. Pb content for 2-4 mm chat ranged between 1,000 to 6,700 mg/kg with an average of 3,600 mg/kg (Fig. 41, A and B). Moving downstream, the weathered chat grains exhibited decreasing Pb content which may be indicative of weathering and sulfide release to the environment, or the slower transport of "heavier" grains due to increased density of residual sulfides (Lewin and Macklin, 1987).

As stated previously, due to local enrichment, zinc levels in ores from Leadwood and Desloge are higher than those found in ores from National, Federal and Bonne Terre mines (Pavlowsky et al., 2010; MDNR, 2008). This study found Zn levels in chat grains between Leadwood to Desloge averaged 3,000 mg/kg in the 2-4 mm tailings and 4,600 mg/kg for the 4-8 mm tailings. Below Flat River, Zn levels steadily declined (Fig. 42, A and B). The unique high Zn geochemical signature of the Leadwood and Desloge piles becomes more evident in this comparison. Near the Flat River confluence, the dilution of the Leadwood mine waste shows a dramatic decrease in Zn content with rising Pb/Zn ratios in the chat grains (Fig. 43). Finally, a comparison of the XRF results for crushed natural and dolomitic "chat" sediments for three downstream location showed natural sediments contained very little Pb while the Pb content of the chat grains was significantly higher (Fig. 44). These examples show chat grains in Big River

channel deposits retain a high residual Pb content. This is concerning because, as grains are weathered and move downstream, heavy metals are at risk for environmental release.

A.



B.

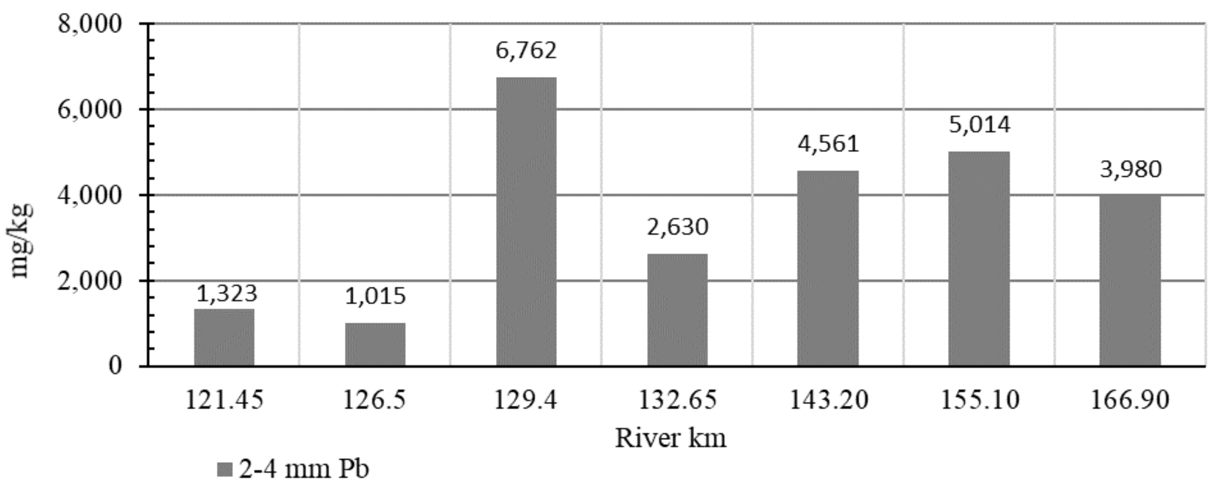
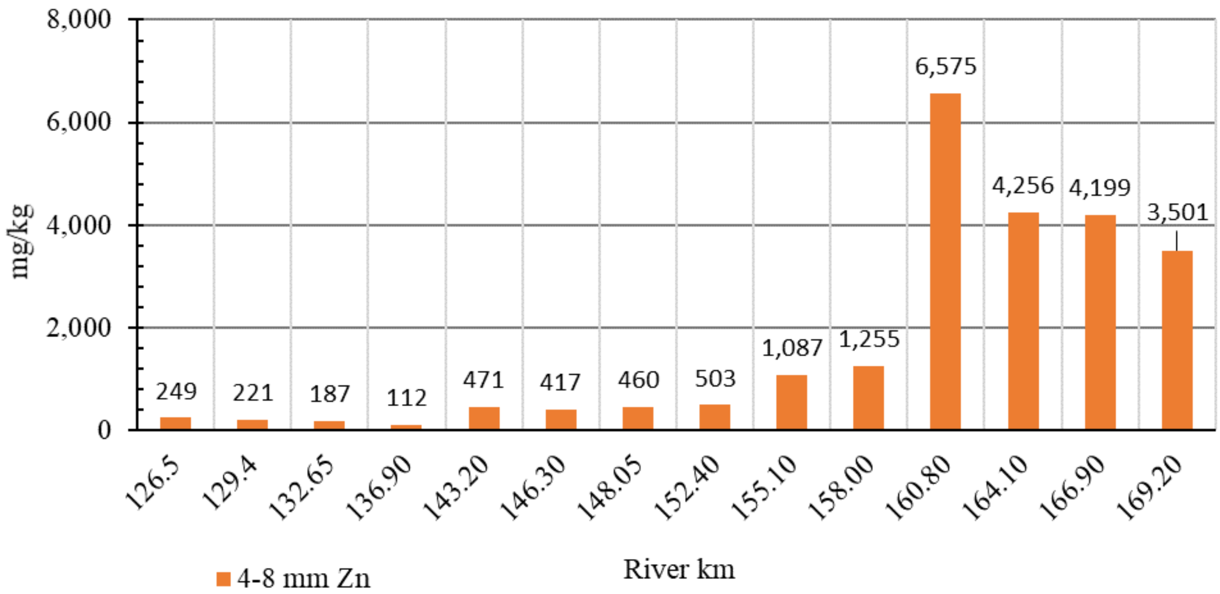


Figure 41: Chat grain Pb content. XRF results for Pb content from selected subsamples of crushed in-channel coarse dolomite "chat" grains by river kilometer. **A.** 4-8 mm chat. **B.** 2-4 mm chat.

A.



B.

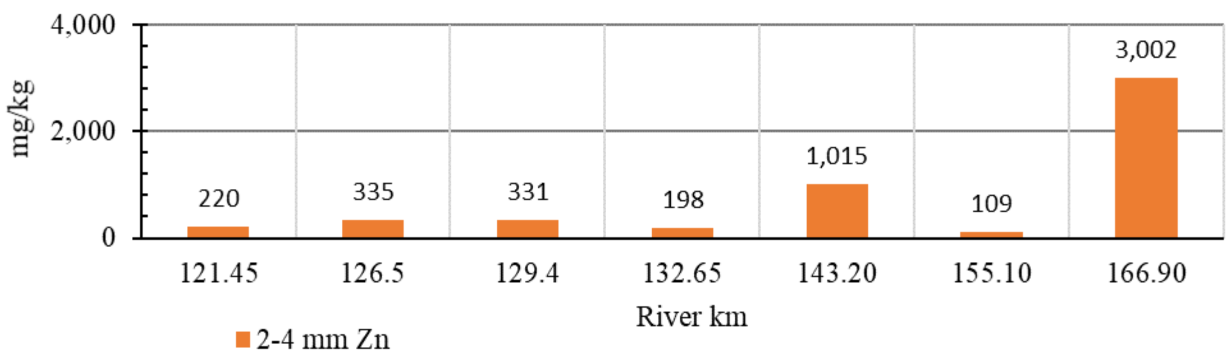
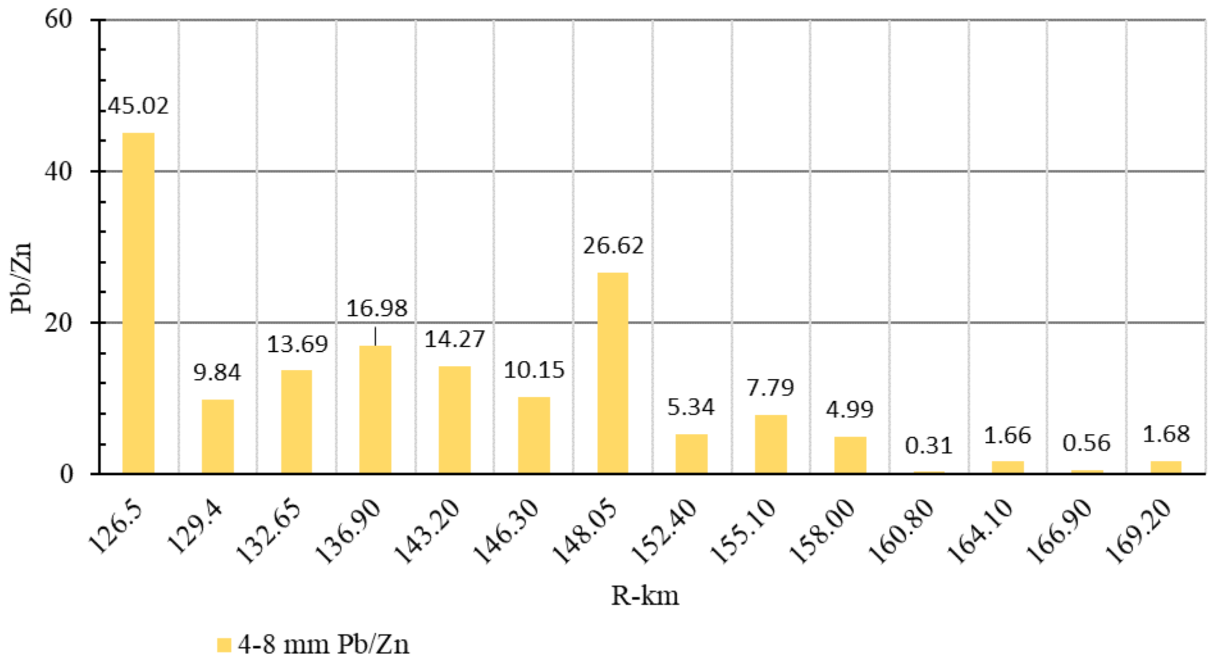


Figure 42: Chat grain Zn content. XRF results for Zn content from selected, crushed chat grains from in-channel gravel bars. **A.** Zn content for 4-8 mm grains. **B**. Zn content for 2-4 mm chat grains.

A.



B.

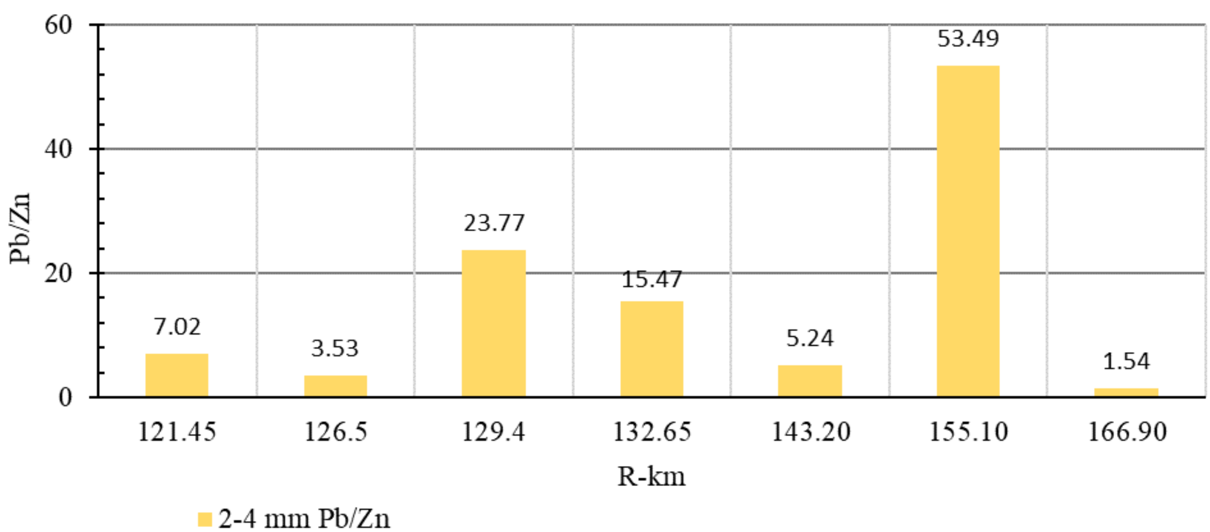
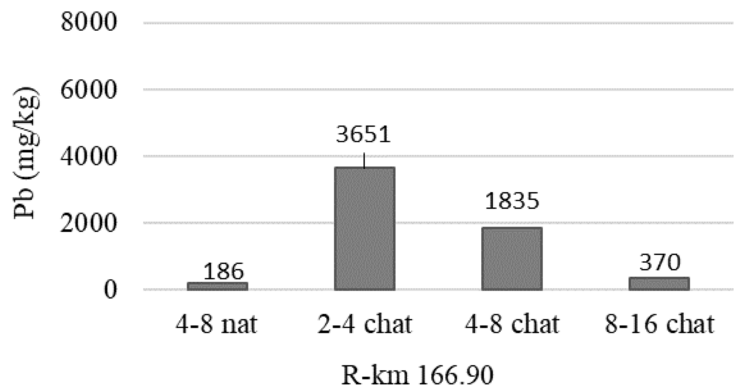
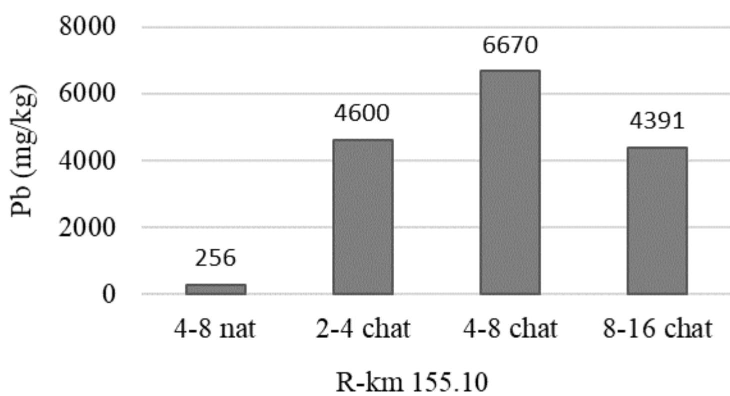


Figure 43: Chat grain Pb/Zn ratios by R-km. **A**. 4-8 mm and **B.** 2-4 mm coarse dolomite grains from gravel bar samples. Pb/Zn ratios are unique for different chat piles and can be used to identify contaminant source.

A.



B.



C.

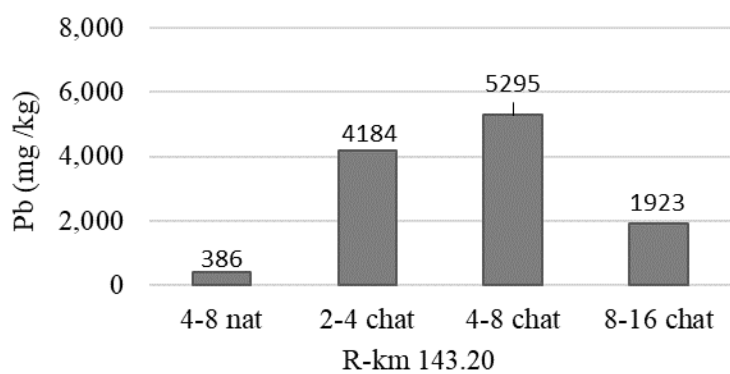


Figure 44: Pb in chat and natural bar sediments. Comparison of Pb content in gravel bar dolomite and natural grains in coarse size fractions (2-16 mm) from three bar sample locations. **A.** Pb content in chat and natural grains at R-km 166.9, near the bar excavation site, downstream from the Leadwood area, but still upstream from Desloge. **B.** Chat and natural coarse grain Pb content at R-km 155.1, at the confluence of Big River and Flat River Creek. **C.** Pb content for chat and natural grains at R-km 143.2, a sharp point-bar location downstream from the confluence with Terre Bleue creek.

CONCLUSIONS

For this study, 92 mine-contaminated channel bar sites in the Big River were sampled between Leadwood and Washington State Park, a distance of almost 80 km. The objectives of this study sought to: 1) quantify the presence and refine the understanding of the distribution and downstream dispersal of coarse (locally called “chat”) mine waste particles (2-16 mm) below mine waste input sites, 2) analyze fine sediment (<2 mm) Ca, Pb, and Zn concentrations in bar deposits, and 3) evaluate the ongoing contamination risk as these coarse sediments are reworked and reactivated within the fluvial system.

Throughout the study area, sediments <2 mm in diameter made up the largest average bulk percent of the gravel bar samples with a median value of 43%, a 25-percentile of 35% and a 75-percentile of 52%. The coarse sediment fractions (2-4, 4-8, and 8-16 mm) averaged from 7% to 20% of the bulk bar sediment composition. When considering size distribution within the gravel bars, there were notable increases in average bulk composition percentages in the chat-sized fractions (2-4 mm, 4-8 mm, and 8-16 mm) below mine input sites where the average 2-4 mm size percentage peaked below Flat River Creek around 19%, the 4-8 mm average peaked just below 21% between Leadwood and Flat River, and the 8-16 mm averaged 16.7% between Leadwood and Flat River, and then averaged 16.8% between Mill Creek and Washington State Park. While the distribution and deposition of sediments in the <32 mm size fraction appears to be most affected by stream energy, stream morphology, and sediment texture, the influx of waste sediments in the mine-affected study area likely contributed to the overall increase in 2-16 mm sediments in downstream bar deposits.

Dolomite percentages in this study represent the presence of mine wastes and can be used as sediment tracers to determine the extent of contamination in the channel (Pavlowsky et al., 2010). The results of this study showed notable decay trends in dolomite percentages downstream from mining inputs. The highest average dolomite percentages in all measured size fractions occurred between Flat River Creek (R-km 155) and the Cabanna Course tributary (R-km 132.5) similar to the patterns reported by Pavlowsky et al. (2010). Dolomite percentages were highest in the <2 mm size fraction, reaching over 60% of the sediments in this size fraction by R-km 145, below the Flat River confluence. Individual dolomite percentages in the 2-4, 4-8, and 8-16 mm fractions peaked at 80, 60, and just over 20% respectively. Concentration peaks occurred for each size fraction as follows: <2 mm at R-km 153-139, 2-4 mm from R-km 155-137, 4-8 mm from R-km 155-142 and 8-16 mm sediments from R-km 155-145. Sediments 2-16 mm dropped near 0% by R-km 115 while sediments <2 mm maintained a presence above 10% throughout the entire study area from Leadwood to Washington State Park. Again, spatial patterns showed deposition of mine wastes was most affected by channel morphology and stream energy.

Flat River Creek represents a significant input of mine tailings 2-16 mm in diameter. The farthest downstream presence of 2-16 mm dolomite sediments represents the oldest sediments released to the river. Dolomite percentages in bar deposits drop below 5% by Mill Creek and an estimate of the transport range of legacy sediments from this source gives a maximum 40 km distance. The Flat River tailings piles were used between the early 1890s and the 1930s, about 120 years ago. The farthest downstream extent of the presence of tailings in the river represents the farthest transport of these legacy sediments, thus, the highest estimate of the transport rate from the 1890s to 2014 would be around 330 meters per year.

The PEC limit for Pb and Zn of 128 mg/kg and 459 mg/kg respectively is exceeded throughout the entire study area. The trends for Pb contamination generally decayed downstream from point sources with the highest readings reaching over 32 times the PEC limit for <2 mm sediments overall and almost 75 times the PEC limit for <0.25 mm size fraction. Zn levels also decayed downstream, however this may be more affected by the unique geochemical signature of the individual mine areas.

Limitations of this study included inconsistent collection methods between years 2013 and 2014 due to changes in collection teams and refinement of research objectives. Bar samples were randomly collected from head, mid and tail bar locations by different teams throughout the study area. While this study provided a good look into dolomite percentages in bar deposits, collecting from the head, middle, and tail of each bar location may give insights into the homogeneity of the bar deposits and provide a more comprehensive picture of overall size and lithology distribution within the bar. Further, there was about a year between collection of the upper reach sediments and the lower reach sediments. High water events and general annual transport may have affected concentrations between years. When analyzing residual Pb and Zn content in weathered chat, there were few downstream chat samples available for XRF analysis as dolomite percentages declined downstream. Further, limited time and resources curtailed the petrographic analysis of chat grains which may have given interesting insights into how these grains weather in the Big River.

Future work might include sampling from head, middle and tail of each bar location to gain a more comprehensive view of coarse mine waste distribution within the bars and to determine if that distribution is affected by bar location. More petrographic analysis, conducted on weathered chat grains to see how sulfide minerals along grain boundaries have begun to

weather and alter, may yield interesting results. Additionally, studying the sphericity and roundness of weathered chat grains in bar and bed deposits might be useful in measuring the amount of weathering the grains endure as in-channel bar deposits and consideration of the research of Larson and Emmons (2021) may yield insights into dissolution rates of the carbonate wastes in the river. It may also be interesting to evaluate the relationship between waste sediment deposition, bar height, channel slope, and water depth. Perhaps this relationship could indicate correlations between different river units, such as riffles, pools, point bars, etc. and mine waste deposition.

In conclusion, chat grains (waste sediments between 2-16 mm in diameter) present a risk to the environment and ecosystem of the Big River. Overall, in the Big River, it is clear that coarse mine sediments make a significant contribution to the composition of channel bar deposits downstream from mine waste sites. The presence of high levels of Pb and Zn in the form of finely disseminated sulfides along the grain boundaries of the carbonate host may represent an ongoing risk as there is a high likelihood that these small crystals could be released into the water column and environment. These sediments have long residence times in the channel and are susceptible to weathering and remobilization during flooding events. They present a significant risk for ongoing Pb and Zn contamination to the Big River for years to come.

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APPENDICES

Appendix A – Bar Sample Location Information

Sediment samples were collected from Big River gravel bars in June, 2013 and July, 2014. The table below shows location measurements for each sample including date collected, GPS position, bar type (center, delta, point, side, riffle, diagonal), sample location within the bar (head, middle, tail), bar height above the water line and water depth at the deepest point near the bar.

Lab Code	Lab #	R-Km/ location	Field Dup	Date	Total Sample Weight(g)	Latitude (Dec Deg)	Longitude (Dec Deg)	Bar Type	Sample Location	Bar Ht. (m)	Water Depth (m)
BGW	1	101.87		7/9/2014	1039	38.087367	-90.679850	side	mid	0.80	1.40
BGW	2	101.75		7/9/2014	1165	38.087683	-90.681150	point	mid		
BGW	3	102.45		7/9/2014	981	38.087333	-90.676533	side	mid	0.20	0.55
BGW	5	102.90		7/9/2014	905	38.088383	-90.669217	point	mid/head	0.80	1.00
BGW	6	103.40		7/9/2014	756	38.088333	-90.663650	point	mid	0.80	1.00
BGW	7	104.15		7/9/2014	1013	38.094000	-90.660900	riffle/point	mid/head	0.30	1.00
BGW	8	104.15	y	7/9/2014	848	38.094000	-90.660900	riffle/point	mid/head	0.80	1.00
BGW	9	104.20		7/9/2014	881	38.094000	-90.661100	point	mid	0.80	1.00
BGW	10	105.05		7/9/2014	770	38.095483	-90.654617	center	mid	0.60	1.30
BGW	11	105.50		7/9/2014	823	38.092167	-90.651367	point	mid	1.00	1.00
BGW	12	105.80		7/9/2014	725	38.089700	-90.652750	side	mid	0.40	1.35
BGW	13	106.20		7/9/2014	919	38.088267	-90.655567	center	tail	1.00	0.70
BGW	15	106.50		7/9/2014	662	38.087100	-90.658433	riffle	mid	0.60	1.00
BGW	16	106.50	y	7/9/2014	901	38.087100	-90.658433	riffle	mid	0.60	1.00
BGW	17	107.00		7/9/2014	1020	38.084233	-90.661867	point	mid	0.62	0.58
BGW	18	107.45		7/9/2014	1169	38.081183	-90.657350	side	tail	0.62	0.58
BGW	19	107.80		7/9/2014	798	38.080950	-90.651750	point	tail	0.30	1.60

Lab Code	Lab #	R-Km/ location	Field Dup	Date	Total Sample Weight(g)	Latitude (Dec Deg)	Longitude (Dec Deg)	Bar Type	Sample Location	Bar Ht. (m)	Water Depth (m)
BGW	21	108.25		7/9/2014	1083	0.000000	0.000000	side/point	mid	0.92	1.40
BGW	23	108.60		7/9/2014	906	38.077550	-90.643117	diagonal	mid	0.40	1.00
BGW	24	108.60	y	7/9/2014	828	38.077550	-90.643117	diagonal	mid	0.40	1.00
BGW	25	109.60		7/9/2014	885	38.075117	-90.635117	point	tail	1.40	0.80
BGW	26	109.75		7/9/2014	929	38.074800	-90.630583		mid	0.40	1.10
BGW	27	110.80		7/9/2014	961	38.072433	-90.613700	side	mid	0.40	1.10
BGW	28	111.45		7/9/2014	966	38.075900	-90.626417	point/riffle	mid	0.40	1.10
BGW	29	111.45	y	7/9/2014	877	38.075900	-90.626417	point/riffle	mid	1.00	1.00
BGW	30	111.50		7/9/2014	845	38.073433	-90.619100	delta	mid/head	0.74	0.65
BGW	31	111.75		7/9/2014	949	38.072433	-90.613700	point	mid	0.70	0.65
BGW	32	112.10		7/9/2014	752	38.069650	-90.612050	riffle	mid	0.40	0.50
BGW	34	112.60	y	7/9/2014	1041	38.065067	-90.612550	riffle	mid	0.40	0.50
BGW	35	112.60		7/9/2014	890	38.065067	-90.612550	riffle	mid	0.20	0.70
BGW	36	113.00		7/9/2014	1165	38.061533	-90.613817	riffle	mid	0.90	0.60
BGW	37	113.50	y	7/9/2014	487	38.058517	-90.617433	riffle	mid	0.60	1.40
BGW	38	113.50		7/9/2014	740	38.058517	-90.617433	riffle	mid	0.60	1.40
BGW	39	115.00		7/9/2014	1403	38.044850	-90.621067	delta	mid	0.40	0.40
BGW	40	115.40		7/8/2014	878	38.042400	-90.620867	point	mid	0.40	0.40
BGW	41	115.80		7/8/2014	962	38.039100	-90.620867	point	mid	0.90	0.50
BGW	42	116.30		7/8/2014	866	38.034817	-90.618967	center	mid/tail	0.00	0.60
BGW	44	116.60		7/8/2014	875	38.030633	-90.617700	point	mid	0.00	0.60
BGW	45	116.60	y	7/8/2014	910	38.030633	-90.617700	point	mid	0.50	1.90
BGW	46	117.50		7/8/2014	699	38.024150	-90.616817	diagonal	mid/tail	0.90	1.50
BGW	47	117.80		7/8/2014	1311	38.021667	-90.616317	bed sediment	-	1.20	1.10
BGW	48	118.15		7/8/2014	886	38.018200	-90.613533	center	mid	0.90	1.20
BGW	49	118.60		7/8/2014	885	38.014650	-90.613767	shadow/point	mid	0.90	1.20
BGW	50	118.60	y	7/8/2014	1056	38.014650	-90.613767	shadow/point	mid	1.30	1.80
BGW	52	118.90		7/8/2014	942	38.013733	-90.615833	riffle	mid	1.30	1.80

Lab Code	Lab #	R-Km/ location	Field Dup	Date	Total Sample Weight(g)	Latitude (Dec Deg)	Longitude (Dec Deg)	Bar Type	Sample Location	Bar Ht. (m)	Water Depth (m)
BGW	53	119.40		7/8/2014	654	38.013100	-90.622083	diagonal/delta	mid	0.20	0.70
BGW	54	120.20		7/8/2014	789	38.010117	-90.628200	point	mid	-	0.70
BGW	55	120.60		7/8/2014	900	38.006550	-90.616400	point	mid	1.80	0.80
BGW	56	120.60	y	7/8/2014	990	38.006550	-90.616400	point	mid	0.40	2.40
BGW	57	121.05		7/8/2014	807	38.007283	-90.621600	side	mid	0.40	2.40
BGW	58	121.45		7/8/2014	742	38.001150	-90.609017	point	mid	0.40	2.40
BGW	59	121.45	y	7/8/2014	844	38.001167	-90.608917	point	mid	1.50	1.00
BGW	60	121.50		7/8/2014	954	0.000000	0.000000	diagonal	mid	0.40	0.70
BGW	62	122.00		7/8/2014	1141	0.000000	0.000000	center	mid	0.72	0.85
BGW	63	123.20		7/8/2014	1095	0.000000	0.000000	riffle/point	tail	0.60	0.60
BGW	64	123.55		7/8/2014	1074	0.000000	0.000000	point	mid	0.60	0.60
BGW	65	124.20		7/8/2014	1136	0.000000	0.000000	point/diagonal	mid	0.68	0.50
BGW	66	124.60		7/8/2014	792	37.988550	-90.609533	center	mid	0.80	0.65
BGW	67	124.60	y	7/8/2014	880	37.988550	-90.609533	center	mid	0.80	0.65
BGW	68	125.05		7/8/2014	875	37.985583	-90.606433	riffle/diagonal	mid	0.40	0.80
BGW	69	125.40		7/8/2014	835	37.983367	-90.603500	center	mid		
BGW	70	126.05		7/8/2014	845	37.984367	-90.597883	diagonal	mid	0.70	0.50
BGW	71	126.50		7/8/2014	979	37.988200	-90.596050	point	mid	0.60	0.50
BGW	72	126.50	y	7/8/2014	1017	37.988200	-90.596050	point	mid	0.69	1.80
BGW	74	127.00		7/8/2014	818	37.990217	-90.591200	point	mid	0.80	0.30
BGW	75	127.30		7/8/2014	839	37.988050	-90.589617	side	mid	0.40	0.60
BGW	76	127.85		7/8/2014	911	37.983433	-90.594883	center	mid	0.40	0.60
BGW	77	128.15		7/8/2014	872	37.982917	-90.595450	side/point	mid	0.50	0.80
BGW	78	128.65		7/8/2014	778	37.979583	-90.593583	point	head	0.80	0.45
BGW	79	128.65	y	7/8/2014	1002	37.979583	-90.593583	point	head	0.30	0.50
BGW	80	128.95		7/8/2014	802	37.970583	-90.591667	shadow/point	tail	0.20	0.70
BGW	81	129.40		7/8/2014	1010	37.970350	-90.591467	bed sediment	-	0.20	0.70
BGW	82	130.10		7/8/2014	778	37.966967	-90.590967	point	tail		

Lab Code	Lab #	R-Km/ location	Field Dup	Date	Total Sample Weight(g)	Latitude (Dec Deg)	Longitude (Dec Deg)	Bar Type	Sample Location	Bar Ht. (m)	Water Depth (m)
BGW	83	130.30		7/8/2014	737	37.964250	-90.590067	riffle	tail	1.10	0.70
BGW	84	130.30	y	7/8/2014	967	37.964250	-90.590067	riffle	tail	0.20	1.00
BGW	85	130.85		7/8/2014	795	37.960967	-90.586583	point	tail	0.40	1.30
BGW	86	131.00		7/8/2014	784	37.962283	-90.583817	point	tail	1.30	0.59
BGW	87	131.40		7/8/2014	842	37.965433	-90.583783	side	mid	0.60	0.52
BGW	88	131.40	y	7/8/2014	662	37.965433	-90.583783	side	mid	0.60	0.52
BGW	89	132.20		7/8/2014	623	37.971533	-90.581050	point	mid	0.20	0.90
BGW	90	132.65	y	7/8/2014	1289	37.969333	-90.577400	riffle	tail		0.50
BGW	91	132.65		7/8/2014	1235	37.969333	-90.577400	riffle	tail	0.60	0.90
BGW	92	132.90		7/8/2014	876	37.967017	-90.575133	delta/riffle	mid	1.60	1.20
BGW	93	133.30		6/14/2013	846	37.964947	-90.572422	side	head	1.60	1.20
BGW	94	133.70		6/14/2013	536	37.966117	-90.569594	point	tail	1.10	2.20
BGW	95	134.00		6/14/2013	513	37.966533	-90.565808	side	mid	0.70	1.50
BGW	96	134.50		6/14/2013	547	37.965658	-90.560511	side	mid	0.20	0.36
BGW	97	135.00		6/14/2013	960	37.965386	-90.555614	side	mid	0.20	0.36
BGW	98	135.50		6/14/2013	777	37.960586	-90.555422	side	head	0.90	1.30
BGW	99	136.00		6/14/2013	1015	37.957214	-90.556997	center	mid	0.70	1.00
BGW	100	136.30		6/14/2013	948	37.954756	-90.556081	center	mid	0.70	1.00
BGW	101	136.90		6/14/2013	796	37.955317	-90.548975	side	tail	1.50	0.70
BGW	102	137.40		6/14/2013	675	37.958606	-90.546533	riffle/side	mid	1.93	1.00
BGW	103	138.00	a	6/14/2013	740	37.963403	-90.544014	side	mid	1.85	1.00
BGW	104	138.50	b	6/14/2013	678	37.966225	-90.540500	center	head	1.98	0.62
BGW	105	139.00		6/14/2013	742	37.967017	-90.535108	side	mid	1.36	0.66
BGW	106	139.50		6/14/2013	910	37.963358	-90.535750	side	head	0.90	0.84
BGW	107	140.00	mid	6/14/2013	811	37.960678	-90.539478	side	mid	1.10	0.90
BGW	108	140.00	head	6/14/2013	770	37.960489	-90.539558	side	head	0.70	
BGW	109	140.80		6/14/2013	1269	37.954417	-90.539619	side	mid	1.00	0.80
BGW	110	141.50		6/14/2013	1082	37.953356	-90.531753	center	mid	0.90	

Lab Code	Lab #	R-Km/ location	Field Dup	Date	Total Sample Weight(g)	Latitude (Dec Deg)	Longitude (Dec Deg)	Bar Type	Sample Location	Bar Ht. (m)	Water Depth (m)
BGW	111	141.85		6/14/2013	1126	37.954058	-90.528500	side	mid	1.63	0.71
BGW	112	142.30		6/14/2013	1090	37.955500	-90.523358	side	head	2.56	1.00
BGW	113	142.80		6/14/2013	903	37.954925	-90.517689	side	head	1.55	1.25
BGW	114	143.20		6/14/2013	1011	37.952872	-90.514678	side	head	1.92	1.10
BGW	115	143.70		6/14/2013	1114	37.948864	-90.517050	side	head	1.73	1.05
BGW	116	144.10		6/14/2013	772	37.945922	-90.518497	side	mid	1.56	1.20
BGW	117	144.50		6/14/2013	980	37.942944	-90.517331	side	mid	0.80	0.80
BGW	118	145.00	a	6/14/2013	1021	37.938417	-90.515444	center	mid	0.30	1.50
BGW	119	145.00	b	6/14/2013	1199	37.938408	-90.515469	center	mid	1.10	0.40
BGW	120	145.40		6/14/2013	1321	37.934961	-90.513378	side	mid	0.3	1.2
BGW	121	145.90		6/14/2013	1057	37.931244	-90.510481	side	mid	0.5	1.3
BGW	122	146.30		6/14/2013	961	37.929408	-90.507642	side	tail	0.5	0.7
BGW	123	146.70		6/14/2013	1118	37.927922	-90.503525	side	tail	0.7	1.1
BGW	124	147.00	a	6/14/2013	962	37.926678	-90.500697	side	tail	0.6	0.75
BGW	125	147.00	b	6/14/2013	947	37.926692	-90.500714	side	tail	1.7	2.4
BGW	126	147.40		6/14/2013	968	37.923958	-90.497483	side	mid	1.3	0.6
BGW	127	148.05		6/14/2013	1031	37.919783	-90.502167	side	mid	0.6	0.7
BGW	128	148.50		6/14/2013	1038	37.919842	-90.507156	side	tail	0.6	0.7
BGW	129	148.90		6/14/2013	1117	37.916986	-90.509817	side	head	0.7	0.6
BGW	130	149.80		6/14/2013	986	37.912392	-90.503400	delta	mid	0.6	0.6
BGW	131	150.20		6/14/2013	1219	37.913242	-90.499539	side	mid	0.6	1
BGW	132	150.70		6/14/2013	1052	37.912447	-90.493886	side	mid	1	0.9
BGW	133	151.70		6/13/2013	794	37.904297	-90.494519	point	mid	0.6	0.6
BGW	134	152.40		6/13/2013	617	37.906189	-90.501239	side	mid	0.6	0.6
BGW	135	152.80		6/13/2013	792	37.906333	-90.506117	side	head	1	1.8
BGW	136	153.30		6/13/2013	787	37.903764	-90.510222	point	tail	1.5	1
BGW	137	153.40		6/13/2013	560	37.902833	-90.510433	side	head	2	1.4
BGW	138	153.70		6/13/2013	767	37.899778	-90.509658	side	mid	0.5	0.8

Lab Code	Lab #	R-Km/ location	Field Dup	Date	Total Sample Weight(g)	Latitude (Dec Deg)	Longitude (Dec Deg)	Bar Type	Sample Location	Bar Ht. (m)	Water Depth (m)
BGW	139	154.70		6/13/2013	578	37.895478	-90.500542	riffle/center	tail	2	1.2
BGW	140	155.10		6/13/2013	672	37.892139	-90.499789	side/delta	mid	1.2	0.45
BGW	141	155.60		6/13/2013	584	37.890594	-90.504711	side	head	0.6	1.5
BGW	142	156.00		6/13/2013	636	37.889706	-90.508911	center	tail	2.3	
BGW	143	156.80		6/13/2013	559	37.890578	-90.518492	side	head	1.15	0.9
BGW	144	157.60		6/13/2013	675	37.892683	-90.526078	point	tail	0.9	0.5
BGW	145	158.00		6/13/2013	640	37.889494	-90.527400	side	tail	1.55	0.7
BGW	146	158.10		6/13/2013	596	37.888447	-90.527558	side	head	1.33	
BGW	147	158.50		6/13/2013	696	37.884936	-90.528264	side	head	1.4	
BGW	148	159.50		6/13/2013	598	37.879875	-90.535992	side	head	0.15	
BGW	149	159.90		6/13/2013	830	37.879772	-90.540606	center	mid	1.65	0.6
BGW	150	160.35		6/13/2013	1118	37.880536	-90.544781	riffle	mid	1.85	0.7
BGW	151	160.80		6/13/2013	785	37.884819	-90.543164	side	head	2.8	1.6
BGW	152	161.40		6/13/2013	829	37.889617	-90.543667	side	mid	2.12	1
BGW	153	162.10		6/13/2013	849	37.893653	-90.549550	riffle	mid	2.84	1.64
BGW	154	162.50	a	6/13/2013	1015	37.893481	-90.553239	side	tail	1.48	0.72
BGW	155	162.50	b	6/13/2013	975	37.893475	-90.553272	side	tail	0.5	0.6
BGW	156	163.00		6/13/2013	858	37.891478	-90.558583	side	mid	0.5	0.8
BGW	157	163.35		6/13/2013	715	37.888964	-90.560139	side	tail	1.4	0.75
BGW	158	163.70		6/13/2013	1014	37.886525	-90.557492	side	tail	0.6	0.75
BGW	159	164.10		6/13/2013	1106	37.883794	-90.554931	center/riffle	mid	1.1	0.65
BGW	160	164.50		6/13/2013	695	37.881017	-90.552883	riffle	mid	0.9	0.7
BGW	161	165.00		6/13/2013	791	37.876922	-90.549347	riffle	head	0.6	0.8
BGW	162	165.20		6/13/2013	983	37.875592	-90.549894	side	mid	1	1.1
BGW	163	165.50		6/12/2013	902	37.874131	-90.552386	side	mid	1.2	1.05
BGW	164	165.90	a	6/13/2013	455	37.872797	-90.556703	center	mid	1.2	1.05
BGW	165	165.90	b	6/12/2013	981	37.872828	-90.556608	center	mid	1	0.9
BGW	166	166.25		6/12/2013	895	37.873478	-90.560089	center	head	1.3	2

Lab Code	Lab #	R-Km/ location	Field Dup	Date	Total Sample Weight(g)	Latitude (Dec Deg)	Longitude (Dec Deg)	Bar Type	Sample Location	Bar Ht. (m)	Water Depth (m)
BGW	167	166.40		6/12/2013	605	37.874933	-90.560350	point	head	1.1	0.75
BGW	168	166.90		6/12/2013	805	37.878731	-90.562211	side	head	0.5	0.75
BGW	169	167.00	a	6/12/2013	717	37.879533	-90.563206	side	mid	0.5	1.1
BGW	170	167.00	b	6/12/2013	654	37.879514	-90.563169	side	mid	0.5	0.8
BGW	171	167.20		6/12/2013	894	37.880094	-90.565458	point	tail	1	1.5
BGW	172	167.50		6/12/2013	923	37.879231	-90.568192	point	mid	0.7	1.7
BGW	173	168.10	a	6/12/2013	765	37.874144	-90.567375	center	tail	1.6	2.1
BGW	174	168.10	b	6/12/2013	407	37.874089	-90.567414	center	tail	1.6	2.1
BGW	175	168.80		6/12/2013	396	37.868017	-90.569200	center	mid	0.8	1.3
BGW	176	168.85		6/12/2013	847	37.867519	-90.569500	center	head		
BGW	177	169.15		6/12/2013	810	37.865247	-90.571842	riffle	head	0.6	0.45
BGW	178	169.20		6/12/2013	555	37.865228	-90.571919				
BGW	179	169.80		6/12/2013	527	37.865503	-90.578019	center	mid		
BGW	180	170.00		6/12/2013	564	37.865992	-90.580839	side		1.2	1.5
BGW	181	170.05		6/12/2013	673	37.866233	-90.581317	side	mid	0.8	1.7

Appendix B: Sediment metal concentrations

Sediment metal concentrations were determined by X-Ray Fluorescence (XRF). Values for Pb, Zn, and Ca were reported within this thesis. Individual bar location results are included here for Pb, Zn, and Ca, as well as Fe and Sr. All values are reported in mg/kg and results for Pb, Zn, and Ca have been adjusted to reflect Aqua Regia values as follows: Pb x 1.09, Zn x 1.27, and Ca x 0.74.

All values in (mg/kg)

LAB ID	R-km	<2 mm Pb	<2 mm Zn	<2 mm Fe	<2 mm Mn	<2 mm Sr	<2 mm Ca	<0.25 mm Pb	<0.25 mm Zn	<0.25 mm Fe	<0.25 mm Mn	<0.25 mm Sr	<0.25 mm Ca
1	101.87	1631	419	17936	1426	44	33162	2363	486	21851	1739	64	38146
2	101.75	436	234	13306	891	26	36685	932	336	18048	1014	76	43568
3	102.45	325	137	10026	493	9	20939	1448	259	18656	1587	50	38477
5	102.90	433	282	12017	693	15	20504	895	183	15193	1506	44	45834
6	103.40	273	91	7437	347	16	15309	750	207	15984	1257	60	36175
7	104.15	230	104	9330	672	10	28432	1488	297	18143	1357	40	40836
9	104.20	441	212	12671	797	16	29903	907	183	16194	1521	42	54233
10	105.05	899	325	15936	1267	21	30480	1518	454	19536	1669	53	36161
11	105.50	336	151	14193	833	14	29202	641	172	13896	1066	37	26959
12	105.80	313	124	9381	776	12	28372	605	163	14514	1320	33	40746
13	106.20	263	95	7946	607	15	22634	947	200	17977	1651	44	58514
15	106.50	768	273	16076	1331	26	38693	1843	434	22484	1855	79	41092
17	107.00	344	119	10325	1031	13	33162	454	131	13816	1376	33	55626
18	107.45	320	177	13187	493	12	14875	813	183	18299	1719	34	53572
19	107.80	518	203	13260	971	17	29093	1195	265	17726	1644	45	43601
21	108.25	384	183	13646	1179	20	41157	991	260	19312	1744	41	47423
23	108.60	436	173	12165	1078	16	37907	652	164	14134	1382	24	40299
25	109.60	350	160	10105	657	19	27749	597	323	16902	1511	30	52242
26	109.75	400	220	14621	964	19	25949	784	321	22748	1989	40	66593
27	110.80	623	437	16268	1397	26	46833	815	221	15667	1410	36	41416

All values in (mg/kg)

LAB ID	R-km	<2 mm Pb	<2 mm Zn	<2 mm Fe	<2 mm Mn	<2 mm Sr	<2 mm Ca	<0.25 mm Pb	<0.25 mm Zn	<0.25 mm Fe	<0.25 mm Mn	<0.25 mm Sr	<0.25 mm Ca
28	111.45	500	276	16977	1426	25	46042	979	320	19783	1778	55	48028
30	111.50	352	175	12486	538	10	18510	869	225	18433	1557	40	49187
31	111.75	437	187	18451	961	12	33506	646	260	16868	1558	38	52586
32	112.10	486	202	14834	1381	28	47895	967	280	17908	1623	47	49422
35	112.60	396	257	21239	1146	17	37643	1133	317	20345	1785	46	51171
36	113.00	497	194	12952	1081	15	41369	1427	430	21775	2223	51	62505
38	113.50	1221	569	27085	908	60	24557	1613	557	23181	1394	76	36176
39	115.00	422	187	15473	943	31	39905	565	197	15601	1361	32	43860
40	115.40	1191	535	22910	1435	46	32173	2401	759	30491	2061	85	36791
41	115.80	778	338	18387	1705	39	51898	898	267	17227	1734	45	55631
42	116.30	435	201	14258	1123	20	40990	823	372	16617	1640	29	48946
44	116.60	460	550	18072	1492	20	62216	656	199	17687	1744	34	63081
46	117.50	407	182	13711	1352	24	57564	368	158	13966	1264	25	51889
47	117.80	431	271	19844	411	14	14036	507	176	16247	1602	33	62746
48	118.15	408	184	14182	1811	26	62948	437	138	13987	1330	27	51359
49	118.60	486	429	17499	1568	21	57744	1538	548	21426	2209	60	46615
52	118.90	474	281	16355	858	17	24837	928	280	18478	1897	42	57467
53	119.40	1075	593	19633	1921	38	37712	2207	783	22926	2061	76	28234
54	120.20	572	312	21111	1832	22	57798	578	197	15019	1398	27	45072
55	120.60	743	315	17251	1613	22	37959	2069	522	22707	1984	72	38813
57	121.05	679	591	18051	1664	21	53558	709	288	16415	1652	34	53221
58	121.45	707	311	20370	2012	37	57577	1013	346	19091	1689	38	43142
60	121.50	665	207	14760	1514	32	52285	1055	231	17705	1832	38	56672
62	122.00	487	254	15328	1596	18	60423	691	231	16808	1588	31	50098
63	123.20	609	377	19252	1963	27	57857	1040	295	20758	2035	39	58390
64	123.55	532	171	18785	2259	26	79400	661	240	19910	2051	38	67892
65	124.20	459	272	19874	1648	26	56980	811	282	17601	1800	33	55134

All values in (mg/kg)

LAB ID	R-km	<2 mm Pb	<2 mm Zn	<2 mm Fe	<2 mm Mn	<2 mm Sr	<2 mm Ca	<0.25 mm Pb	<0.25 mm Zn	<0.25 mm Fe	<0.25 mm Mn	<0.25 mm Sr	<0.25 mm Ca
66	124.60	606	231	17285	1974	26	62123	1006	464	20132	1752	53	45092
68	125.05	788	423	17523	1490	30	52261	618	567	14533	1183	21	46523
69	125.40	669	258	25079	1737	31	61989	1474	435	21558	2236	61	58032
70	126.05	940	638	19586	1867	36	43109	1946	827	22606	2089	69	36207
71	126.50	1047	410	21925	1391	35	50583	2007	550	20150	868	73	27560
74	127.00	803	254	17659	1943	24	58840	1300	397	21214	2161	49	52311
75	127.30	1009	668	20261	1363	31	42588	1047	395	18052	1561	39	44700
76	127.85	972	462	47376	2527	26	65322	764	329	18355	1662	39	43127
77	128.15	528	286	18248	1919	23	67803	695	246	18605	1783	31	58552
78	128.65	871	328	21560	2396	35	70293	1791	569	22729	2110	66	46267
80	128.95	1139	549	21956	1650	39	52210	1399	545	21375	1497	56	52318
81	129.40	650	287	23910	2659	29	93378	685	244	19745	1990	39	78241
82	130.10	646	292	18332	2099	35	68561	1623	517	23177	2139	70	46673
83	130.30	1303	721	19628	1909	40	49368	1245	425	18963	1871	43	48077
85	130.85	592	243	21204	2029	33	75817	591	331	14431	1593	33	61149
86	131.00	1413	665	21344	2184	44	41979	1869	618	22797	2128	59	35075
87	131.40	554	240	20590	2225	22	90895	1012	377	19083	1919	44	57055
89	132.20	731	443	24081	2375	35	73316	790	275	16861	1682	34	48415
91	132.65	734	323	19832	2479	33	70805	749	436	16898	1822	36	57707
92	132.90	1038	898	20771	2270	44	50791	1926	611	23559	2680	73	53165
93	133.30	738	409	23323	2254	36	67814	1923	807	34728	4268	57	80841
94	133.70	476	246	16030	1566	27	58264	2488	1147	45851	5771	59	102583
95	134.00	549	284	17008	1890	28	63922	2068	732	40059	5274	50	105296
96	134.50	1004	829	22020	2015	40	55909	2765	908	40736	5244	58	96786
97	135.00	1141	541	25990	2856	29	71954	2736	1034	55723	8001	53	118878
98	135.50	809	853	20804	2492	34	80390	3027	1207	59063	8815	59	126865
99	136.00	871	415	35073	2569	40	90769	2896	1286	56182	8194	59	126458

All values in (mg/kg)

LAB ID	R-km	<2 mm Pb	<2 mm Zn	<2 mm Fe	<2 mm Mn	<2 mm Sr	<2 mm Ca	<0.25 mm Pb	<0.25 mm Zn	<0.25 mm Fe	<0.25 mm Mn	<0.25 mm Sr	<0.25 mm Ca
100	136.30	364	253	18040	1964	34	73816	2711	1227	53171	8328	60	112880
101	136.90	735	405	26048	2485	36	93505	1582	766	32507	3982	49	79472
102	137.40	801	413	25736	3195	40	91920	3015	1116	57357	8869	60	120126
103	138.00	548	363	17970	1842	30	68930	2982	1205	56334	9162	60	109268
104	138.50	595	249	19070	2587	32	100231	2696	1098	51436	8123	55	123721
105	139.00	1028	2383	31391	3129	39	96785	2594	2922	44934	6394	57	108990
106	139.50	1693	486	37437	3632	57	128630	3958	1393	64695	11089	63	122714
107	140.00	955	540	37171	2776	32	90690	3324	1013	57694	8412	59	131039
109	140.80	458	264	17674	2046	34	84845	3129	987	50568	7508	58	114565
110	141.50	872	511	35933	3224	24	71249	3678	1204	58310	9065	73	115198
111	141.85	738	349	22460	2084	21	77684	2222	916	48149	7189	60	112868
112	142.30	977	598	34409	3312	35	101303	3245	1223	55813	8685	63	102907
113	142.80	748	380	22025	2624	30	73955	2929	1058	55538	7577	55	107601
114	143.20	640	396	21475	2588	32	83334	3176	1134	65776	10127	58	124234
115	143.70	431	222	16454	1866	25	75543	2656	981	58025	8227	63	104350
116	144.10	340	187	13307	1192	22	43745	1723	775	38963	5096	52	79078
117	144.50	1142	466	27444	3312	41	108076	2878	873	45793	7009	54	126261
118	145.00	1472	493	30278	4438	44	135223	3508	1004	44918	7167	56	138165
120	145.40	1069	504	29204	2921	36	97257	1665	593	34504	4536	53	116574
121	145.90	1559	890	47726	3850	41	107817	4092	1171	46124	6589	59	150222
122	146.30	1717	1039	28926	3302	45	91194	3125	990	30516	3407	69	88936
123	146.70	838	533	21234	2183	34	97501	3690	1250	45848	7088	58	156889
124	147.00	968	505	26486	2623	30	101270	3213	1277	39419	6792	55	128132
126	147.40	1984	1190	28597	3192	51	98009	3272	1282	32349	4085	52	91949
127	148.05	1728	1086	28293	3061	50	85019	3702	1254	41057	6066	68	125922
128	148.50	1315	718	27313	3118	47	114491	3852	1749	46110	6436	70	125702
129	148.90	1170	765	25424	3230	36	100566	4363	1452	44375	6734	63	135317

All values in (mg/kg)

LAB ID	R-km	<2 mm Pb	<2 mm Zn	<2 mm Fe	<2 mm Mn	<2 mm Sr	<2 mm Ca	<0.25 mm Pb	<0.25 mm Zn	<0.25 mm Fe	<0.25 mm Mn	<0.25 mm Sr	<0.25 mm Ca
130	149.80	2054	970	26586	3211	53	86095	5140	1201	41014	5425	57	130031
131	150.20	1315	5772	29044	2763	42	83252	3345	1461	37410	4984	61	117130
132	150.70	1478	1015	26193	3123	52	91986	3814	1247	43215	6182	56	140034
133	151.70	1303	1142	26952	4008	43	113397	4577	1800	46056	7239	64	143055
134	152.40	1589	799	29437	3186	34	123066	2572	1289	37002	4775	52	130462
135	152.80	1341	1060	34818	2634	57	107780	3447	1836	41943	5738	62	140587
136	153.30	907	784	24358	2955	47	127777	4978	2389	43622	6228	64	133778
137	153.40	2128	1287	41501	4717	58	118740	5701	1314	39777	4618	67	130636
138	153.70	1675	1598	36629	3410	58	101596	4147	2286	40741	5825	61	140870
139	154.70	1545	1539	47217	1961	27	51835	3018	1628	45900	6450	56	103814
140	155.10	2178	671	33366	3765	46	94426	5912	779	69533	9544	58	139000
141	155.60	938	899	23852	2220	36	98931	3957	2685	37884	4845	63	134673
142	156.00	835	1853	16632	1896	36	79073	3191	2687	33382	4377	61	139123
143	156.80	1239	1745	21900	2409	34	99089	3962	2784	32936	4596	66	150668
144	157.60	857	1391	15934	1677	33	70166	3018	2323	28968	4090	54	122855
145	158.00	1679	1097	30245	2391	43	104230	5534	2866	33945	5132	67	144351
146	158.10	1514	1529	17359	1771	36	56318	4186	2513	27417	3521	54	123157
147	158.50	4094	3040	22598	2031	46	78176	9549	3544	34622	4224	65	139300
148	159.50	756	1539	21062	2281	32	87552	1908	1935	25252	2745	46	101528
149	159.90	955	1231	25879	2481	42	83895	3017	2809	32218	4096	63	128432
150	160.35	633	1448	16665	2055	36	76059	2504	3253	30448	3747	58	126696
151	160.80	1158	1462	21333	1584	50	49026	3711	3636	34734	4078	75	139391
152	161.40	687	1770	16276	1231	38	25426	1533	1592	22032	1954	43	60549
153	162.10	2520	2747	29772	2497	57	80562	4272	4607	32840	3796	68	124953
154	162.50	934	2972	16212	1513	33	56735	3285	4359	27197	3264	49	130731
156	163.00	511	3856	15525	1272	21	55694	3348	3383	27598	3099	55	127004
157	163.35	1654	2209	20062	2231	37	97098	3082	3353	30164	3844	52	144473

All values in (mg/kg)

LAB ID	R-km	<2 mm Pb	<2 mm Zn	<2 mm Fe	<2 mm Mn	<2 mm Sr	<2 mm Ca	<0.25 mm Pb	<0.25 mm Zn	<0.25 mm Fe	<0.25 mm Mn	<0.25 mm Sr	<0.25 mm Ca
158	163.70	1273	1753	24097	2619	41	84985	2362	2462	29411	3501	56	76776
159	164.10	2402	7371	19607	1469	48	58537	6855	11435	33702	3918	71	146085
160	164.50	1226	3240	17305	1544	41	53889	4628	8222	30567	2797	66	91867
161	165.00	1429	2370	17785	1438	45	40343	6835	10391	32896	3741	63	125581
162	165.20	1047	2032	16448	1525	37	49485	6517	5093	38126	4439	72	113668
163	165.50	1050	1584	21355	1511	33	74471	5364	7655	35299	4063	65	129861
164	165.90	3311	7615	18865	1141	46	32804	8598	8777	23190	1623	59	54439
166	166.25	1927	4759	14697	1011	40	39122	5284	5287	21308	1572	70	44901
167	166.40	1117	3285	20379	2601	43	59978	2963	4940	28220	2620	53	105477
168	166.90	883	1273	17764	1208	43	23397	4166	4294	29415	2588	73	78608
169	167.00	1222	3353	13225	1113	26	48705	3145	6757	27513	2327	55	89466
171	167.20	647	1344	15385	1216	21	61453	1720	3412	26727	2385	54	100417
172	167.50	600	1261	11031	887	20	51820	1768	4488	23688	1973	40	84406
173	168.10	775	3514	14299	1149	27	31001	3322	3585	29218	2774	68	69507
175	168.80	506	585	13391	820	32	18737	921	1295	21249	1453	52	21650
176	168.85	634	2404	9932	644	24	38578	2832	4559	22869	1650	44	61950
177	169.15	840	3970	12347	835	17	45315	3039	6055	26970	2483	50	88843
178	169.20	391	474	13804	611	16	32639	2700	3625	27328	1949	40	79681
179	169.80	996	3106	13895	866	25	26095	4026	2272	18487	1346	41	35840
180	170.00	744	1227	12375	701	18	29781	3324	3616	29876	1903	51	53498
181	170.05	481	377	9791	591	8	13566	803	845	13167	651	21	21783

Appendix C – Sample Bulk Percentages by Size Fraction

Sediment samples were weighed and sieved into the following size fractions: >32 mm, 16-32 mm, 8-16 mm, 4-8 mm, 2-4 mm and <2 mm. Sediments larger than 32 mm were removed from the samples therefore all total weight values below are for bar sediments <32 mm. After XRF analysis, the <2 mm samples were further sieved and separated into < 0.25 mm and 0.25-2 mm. Bulk percentages were calculated by weight in grams divided by the total sample weight, (less the > 32mm fraction.

Lab #	R-Km/ location	Date	Tot Sample Weight (g)	16-32 mm (g)	8-16 mm (g)	4-8 mm (g)	2-4 mm (g)	<2 mm (g)	<0.25 mm (g)	16-32 mm mass %	8-16 mm mass %	4-8 mm mass %	2-4 mm mass %	<2 mm mass %	<0.25 mm mass %
1	101.87	7/9/2014	1039	96	185	229	174	348	95	9.24	17.81	22.04	16.75	33.49	9.11
2	101.75	7/9/2014	1200	216	192	190	125	479	35	18.00	16.00	15.83	10.42	39.92	2.93
3	102.45	7/9/2014	868	260	81	86	79	360	11	29.95	9.33	9.91	9.10	41.47	1.22
5	102.90	7/9/2014	905	49	100	96	72	582	35	5.41	11.05	10.61	7.96	64.31	3.89
6	103.40	7/9/2014	756	86	143	144	74	309	16	11.38	18.92	19.05	9.79	40.87	2.08
7	104.15	7/9/2014	1013	32	125	144	144	566	29	3.16	12.34	14.22	14.22	55.87	2.81
8	104.15	7/9/2014	848	59	165	188	124	307	10	6.96	19.46	22.17	14.62	36.20	1.13
9	104.20	7/9/2014	861	44	63	120	99	536	61	5.11	7.32	13.94	11.50	62.25	7.08
10	105.05	7/9/2014	770	78	145	143	102	293	18	10.13	18.83	18.57	13.25	38.05	2.31
11	105.50	7/9/2014	823	49	189	186	105	286	9	5.95	22.96	22.60	12.76	34.75	1.08
12	105.80	7/9/2014	725	45	66	67	43	502	41	6.21	9.10	9.24	5.93	69.24	5.69
13	106.20	7/9/2014	919	79	151	126	84	473	21	8.60	16.43	13.71	9.14	51.47	2.32
15	106.50	7/9/2014	662	150	146	114	77	172	11	22.66	22.05	17.22	11.63	25.98	1.60
16	106.50	7/9/2014	901	125	172	171	108	322	24	13.87	19.09	18.98	11.99	35.74	2.72
17	107.00	7/9/2014	1020	120	170	122	80	523	15	11.76	16.67	11.96	7.84	51.27	1.51
18	107.45	7/9/2014	1169	220	191	133	81	542	24	18.82	16.34	11.38	6.93	46.36	2.09
19	107.80	7/9/2014	798	97	165	178	125	229	16	12.16	20.68	22.31	15.66	28.70	2.04
21	108.25	7/9/2014	1083	140	270	289	198	179	7	12.93	24.93	26.69	18.28	16.53	0.67

Lab #	R-Km/ location	Date	Tot Sample Weight (g)	16-32 mm (g)	8-16 mm (g)	4-8 mm (g)	2-4 mm (g)	<2 mm (g)	<0.25 mm (g)	16-32 mm mass %	8-16 mm mass %	4-8 mm mass %	2-4 mm mass %	<2 mm mass %	<0.25 mm mass %
23	108.60	7/9/2014	906	36	183	179	140	364	54	3.97	20.20	19.76	15.45	40.18	5.95
24	108.60	7/9/2014	828	81	122	158	132	333	41	9.78	14.73	19.08	15.94	40.22	4.94
25	109.60	7/9/2014	885	47	68	97	94	575	40	5.31	7.68	10.96	10.62	64.97	4.53
26	109.75	7/9/2014	878	143	219	200	127	185	6	16.29	24.94	22.78	14.46	21.07	0.71
27	110.80	7/9/2014	961	90	244	155	68	402	90	9.37	25.39	16.13	7.08	41.83	9.32
28	111.45	7/9/2014	918	79	232	158	79	364	26	8.61	25.27	17.21	8.61	39.65	2.83
29	111.45	7/9/2014	877	128	126	123	75	421	14	14.60	14.37	14.03	8.55	48.00	1.65
30	111.50	7/9/2014	845	30	77	133	137	465	12	3.55	9.11	15.74	16.21	55.03	1.47
31	111.75	7/9/2014	949	25	113	123	151	531	11	2.63	11.91	12.96	15.91	55.95	1.18
32	112.10	7/9/2014	685	83	127	100	50	327	30	12.12	18.54	14.60	7.30	47.74	4.34
34	112.60	7/9/2014	1041	112	166	150	114	494	20	10.76	15.95	14.41	10.95	47.45	1.89
35	112.60	7/9/2014	829	104	154	117	109	341	19	12.55	18.58	14.11	13.15	41.13	2.26
36	113.00	7/9/2014	1165	214	216	141	104	486	44	18.37	18.54	12.10	8.93	41.72	3.74
37	113.50	7/9/2014	487	40	35	32	29	350	27	8.21	7.19	6.57	5.95	71.87	5.47
38	113.50	7/9/2014	740	144	137	58	56	342	28	19.46	18.51	7.84	7.57	46.22	3.81
39	115.00	7/9/2014	1349	117	157	195	167	707	37	8.67	11.64	14.46	12.38	52.41	2.75
40	115.40	7/8/2014	878	176	150	100	102	347	113	20.05	17.08	11.39	11.62	39.52	12.91
41	115.80	7/8/2014	962	60	132	185	175	405	8	6.24	13.72	19.23	18.19	42.10	0.84
42	116.30	7/8/2014	866	40	164	133	98	427	21	4.62	18.94	15.36	11.32	49.31	2.37
44	116.60	7/8/2014	875	115	133	134	89	403	29	13.14	15.20	15.31	10.17	46.06	3.31
45	116.60	7/8/2014	910	116	91	99	68	534	19	12.75	10.00	10.88	7.47	58.68	2.10
46	117.50	7/8/2014	699	7	82	109	95	408	24	1.00	11.73	15.59	13.59	58.37	3.42
47	117.80	7/8/2014	1311	125	143	164	147	725	41	9.53	10.91	12.51	11.21	55.30	3.11
48	118.15	7/8/2014	886	21	31	37	29	766	73	2.37	3.50	4.18	3.27	86.46	8.24
49	118.60	7/8/2014	885	76	76	84	88	562	18	8.59	8.59	9.49	9.94	63.50	2.02
50	118.60	7/8/2014	1056	85	101	129	99	646	25	8.05	9.56	12.22	9.38	61.17	2.35
52	118.90	7/8/2014	942	65	101	84	64	627	60	6.90	10.72	8.92	6.79	66.56	6.39
53	119.40	7/8/2014	654	6	26	111	111	402	58	0.92	3.98	16.97	16.97	61.47	8.83

Lab #	R-Km/ location	Date	Tot Sample Weight (g)	16-32 mm (g)	8-16 mm (g)	4-8 mm (g)	2-4 mm (g)	<2 mm (g)	<0.25 mm (g)	16-32 mm mass %	8-16 mm mass %	4-8 mm mass %	2-4 mm mass %	<2 mm mass %	<0.25 mm mass %
54	120.20	7/8/2014	789	28	119	152	112	373	18	3.55	15.08	19.26	14.20	47.28	2.31
55	120.60	7/8/2014	900	82	167	122	74	447	17	9.11	18.56	13.56	8.22	49.67	1.93
56	120.60	7/8/2014	990	227	260	173	84	248	10	22.93	26.26	17.47	8.48	25.05	1.00
57	121.05	7/8/2014	807	64	71	55	59	556	14	7.93	8.80	6.82	7.31	68.90	1.68
58	121.45	7/8/2014	742	40	123	135	142	297	29	5.39	16.58	18.19	19.14	40.03	3.95
59	121.45	7/8/2014	844	132	161	140	121	286	34	15.64	19.08	16.59	14.34	33.89	4.04
60	121.50	7/8/2014	907	176	69	42	26	592	73	19.40	7.61	4.63	2.87	65.27	8.07
62	122.00	7/8/2014	1070	80	146	158	134	547	17	7.48	13.64	14.77	12.52	51.12	1.61
63	123.20	7/8/2014	1095	135	240	173	141	401	20	12.33	21.92	15.80	12.88	36.62	1.83
64	123.55	7/8/2014	1074	24	93	149	211	587	5	2.23	8.66	13.87	19.65	54.66	0.48
65	124.20	7/8/2014	1109	93	220	131	109	557	23	8.39	19.84	11.81	9.83	50.23	2.05
66	124.60	7/8/2014	792	159	124	100	72	335	10	20.08	15.66	12.63	9.09	42.30	1.24
67	124.60	7/8/2014	880	82	115	115	85	480	17	9.32	13.07	13.07	9.66	54.55	1.93
68	125.05	7/8/2014	875	196	222	94	43	316	55	22.40	25.37	10.74	4.91	36.11	6.24
69	125.40	7/8/2014	815	39	113	185	181	293	9	4.79	13.87	22.70	22.21	35.95	1.12
70	126.05	7/8/2014	800	219	153	109	77	236	16	27.38	19.13	13.63	9.63	29.50	2.01
71	126.50	7/8/2014	979	120	156	162	144	393	79	12.26	15.93	16.55	14.71	40.14	8.09
72	126.50	7/8/2014	1015	136	164	160	128	418	30	13.40	16.16	15.76	12.61	41.18	2.94
74	127.00	7/8/2014	818	36	185	274	137	183	9	4.40	22.62	33.50	16.75	22.37	1.12
75	127.30	7/8/2014	839	73	142	101	76	441	122	8.70	16.92	12.04	9.06	52.56	14.49
76	127.85	7/8/2014	860	71	133	183	127	338	22	8.26	15.47	21.28	14.77	39.30	2.56
77	128.15	7/8/2014	872	70	110	115	107	465	9	8.03	12.61	13.19	12.27	53.33	1.07
78	128.65	7/8/2014	778	123	96	97	115	342	21	15.81	12.34	12.47	14.78	43.96	2.67
79	128.65	7/8/2014	1002	111	182	171	154	377	20	11.08	18.16	17.07	15.37	37.62	1.95
80	128.95	7/8/2014	768	93	161	76	50	382	64	12.11	20.96	9.90	6.51	49.74	8.29
81	129.40	7/8/2014	1010	38	202	241	211	317	8	3.76	20.00	23.86	20.89	31.39	0.82
82	130.10	7/8/2014	778	138	132	103	58	344	11	17.74	16.97	13.24	7.46	44.22	1.39
83	130.30	7/8/2014	737	0	21	13	15	689	65	0.00	2.85	1.76	2.04	93.49	8.84

Lab #	R-Km/ location	Date	Tot Sample Weight (g)	16-32 mm (g)	8-16 mm (g)	4-8 mm (g)	2-4 mm (g)	<2 mm (g)	<0.25 mm (g)	16-32 mm mass %	8-16 mm mass %	4-8 mm mass %	2-4 mm mass %	<2 mm mass %	<0.25 mm mass %
84	130.30	7/8/2014	967	223	252	220	127	147	25	23.06	26.06	22.75	13.13	15.20	2.58
85	130.85	7/8/2014	795	96	92	77	98	427	13	12.08	11.57	9.69	12.33	53.71	1.58
86	131.00	7/8/2014	784	4	60	183	199	338	40	0.51	7.65	23.34	25.38	43.11	5.13
87	131.40	7/8/2014	842	18	51	60	124	583	15	2.14	6.06	7.13	14.73	69.24	1.78
88	131.40	7/8/2014	662	48	78	56	51	427	35	7.25	11.78	8.46	7.70	64.50	5.30
89	132.20	7/8/2014	623	14	70	116	96	327	14	2.25	11.24	18.62	15.41	52.49	2.30
90	132.65	7/8/2014	1247	248	227	158	139	471	43	19.89	18.20	12.67	11.15	37.77	3.43
91	132.65	7/8/2014	1201	223	168	142	114	550	97	18.57	13.99	11.82	9.49	45.80	8.12
92	132.90	7/8/2014	876	9	59	114	161	531	82	1.03	6.74	13.01	18.38	60.62	9.41
93	133.30	6/14/2013	797	34	40	48	51	620	76	4.27	5.02	6.02	6.40	77.79	9.56
94	133.70	6/14/2013	536	4	5	12	15	497	21	0.75	0.93	2.24	2.80	92.72	3.85
95	134.00	6/14/2013	513	35	69	63	66	277	25	6.82	13.45	12.28	12.87	54.00	4.84
96	134.50	6/14/2013	547	104	85	76	81	198	27	19.01	15.54	13.89	14.81	36.20	4.87
97	135.00	6/14/2013	960	9	39	54	93	762	66	0.94	4.06	5.63	9.69	79.38	6.85
98	135.50	6/14/2013	777	49	81	101	119	424	22	6.31	10.42	13.00	15.32	54.57	2.84
99	136.00	6/14/2013	1015	35	95	129	157	596	15	3.45	9.36	12.71	15.47	58.72	1.43
100	136.30	6/14/2013	948	89	142	130	97	481	19	9.39	14.98	13.71	10.23	50.74	2.00
101	136.90	6/14/2013	796	70	95	171	164	294	56	8.79	11.93	21.48	20.60	36.93	6.99
102	137.40	6/14/2013	675	58	102	91	82	340	13	8.59	15.11	13.48	12.15	50.37	1.96
103	138.00	6/14/2013	740	0	52	148	201	337	25	0.00	7.03	20.00	27.16	45.54	3.36
104	138.50	6/14/2013	678	15	17	29	50	571	18	2.21	2.51	4.28	7.37	84.22	2.67
105	139.00	6/14/2013	742	14	97	204	227	196	26	1.89	13.07	27.49	30.59	26.42	3.50
106	139.50	6/14/2013	870	11	63	160	293	340	32	1.26	7.24	18.39	33.68	39.08	3.63
107	140.00	6/14/2013	811	169	194	171	106	170	15	20.84	23.92	21.09	13.07	20.96	1.79
108	140.00	6/14/2013	770	0	76	154	267	270	21	0.00	9.87	20.00	34.68	35.06	2.78
109	140.80	6/14/2013	1269	93	151	236	178	613	16	7.33	11.90	18.60	14.03	48.31	1.28
110	141.50	6/14/2013	1082	62	106	173	177	561	18	5.73	9.80	15.99	16.36	51.85	1.62

Lab #	R-Km/ location	Date	Tot Sample Weight (g)	16-32 mm (g)	8-16 mm (g)	4-8 mm (g)	2-4 mm (g)	<2 mm (g)	<0.25 mm (g)	16-32 mm mass %	8-16 mm mass %	4-8 mm mass %	2-4 mm mass %	<2 mm mass %	<0.25 mm mass %
111	141.85	6/14/2013	1126	29	44	97	120	836	29	2.58	3.91	8.61	10.66	74.25	2.61
112	142.30	6/14/2013	1090	114	132	195	136	516	14	10.46	12.11	17.89	12.48	47.34	1.30
113	142.80	6/14/2013	864	72	91	153	176	373	18	8.33	10.53	17.71	20.37	43.17	2.08
114	143.20	6/14/2013	1011	100	160	274	201	276	20	9.89	15.83	27.10	19.88	27.30	1.95
115	143.70	6/14/2013	1083	221	123	105	80	556	25	20.41	11.36	9.70	7.39	51.34	2.34
116	144.10	6/14/2013	772	42	79	136	117	392	36	5.44	10.23	17.62	15.16	50.78	4.64
117	144.50	6/14/2013	957	130	212	212	111	259	20	13.58	22.15	22.15	11.60	27.06	2.06
118	145.00	6/14/2013	1021	53	38	249	305	372	28	5.19	3.72	24.39	29.87	36.43	2.76
119	145.00	6/14/2013	1199	35	42	284	371	464	19	2.92	3.50	23.69	30.94	38.70	1.60
120	145.40	6/14/2013	1321	25	115	312	228	637	123	1.89	8.71	23.62	17.26	48.22	9.32
121	145.90	6/14/2013	1057	12	33	134	341	533	16	1.14	3.12	12.68	32.26	50.43	1.53
122	146.30	6/14/2013	961	110	133	231	164	323	40	11.45	13.84	24.04	17.07	33.61	4.20
123	146.70	6/14/2013	1118	55	78	166	194	620	25	4.92	6.98	14.85	17.35	55.46	2.20
124	147.00	6/14/2013	962	0	5	15	47	893	27	0.00	0.52	1.56	4.89	92.83	2.77
125	147.00	6/14/2013	947	0	3	26	81	838	23	0.00	0.32	2.75	8.55	88.49	2.46
126	147.40	6/14/2013	968	128	197	176	107	356	36	13.22	20.35	18.18	11.05	36.78	3.77
127	148.05	6/14/2013	1031	176	258	248	175	172	23	17.07	25.02	24.05	16.97	16.68	2.25
128	148.50	6/14/2013	990	143	156	156	118	412	13	14.44	15.76	15.76	11.92	41.62	1.29
129	148.90	6/14/2013	1076	84	115	249	246	379	18	7.81	10.69	23.14	22.86	35.22	1.69
130	149.80	6/14/2013	986	171	199	270	193	147	18	17.34	20.18	27.38	19.57	14.91	1.80
131	150.20	6/14/2013	1219	126	168	433	256	233	25	10.34	13.78	35.52	21.00	19.11	2.09
132	150.70	6/14/2013	1052	66	202	281	209	293	21	6.27	19.20	26.71	19.87	27.85	1.95
133	151.70	6/13/2013	794	9	75	164	181	363	15	1.13	9.45	20.65	22.80	45.72	1.84
134	152.40	6/13/2013	617	16	72	110	113	310	25	2.59	11.67	17.83	18.31	50.24	4.13
135	152.80	6/13/2013	792	0	6	45	150	592	14	0.00	0.76	5.68	18.94	74.75	1.78
136	153.30	6/13/2013	787	29	34	94	156	473	14	3.68	4.32	11.94	19.82	60.10	1.74
137	153.40	6/13/2013	560	52	129	145	127	105	19	9.29	23.04	25.89	22.68	18.75	3.38
138	153.70	6/13/2013	767	95	58	122	185	306	18	12.39	7.56	15.91	24.12	39.90	2.32

Lab #	R-Km/ location	Date	Tot Sample Weight (g)	16-32 mm (g)	8-16 mm (g)	4-8 mm (g)	2-4 mm (g)	<2 mm (g)	<0.25 mm (g)	16-32 mm mass %	8-16 mm mass %	4-8 mm mass %	2-4 mm mass %	<2 mm mass %	<0.25 mm mass %
139	154.70	6/13/2013	578	0	0	17	75	483	35	0.00	0.00	2.94	12.98	83.56	5.97
140	155.10	6/13/2013	672	74	103	123	224	146	20	11.01	15.33	18.30	33.33	21.73	2.99
141	155.60	6/13/2013	584	19	78	97	97	294	23	3.25	13.36	16.61	16.61	50.34	3.93
142	156.00	6/13/2013	636	33	92	121	118	272	15	5.19	14.47	19.03	18.55	42.77	2.31
143	156.80	6/13/2013	559	61	82	143	113	159	14	10.91	14.67	25.58	20.21	28.44	2.52
144	157.60	6/13/2013	675	9	41	141	171	311	28	1.33	6.07	20.89	25.33	46.07	4.16
145	158.00	6/13/2013	640	27	59	179	199	174	16	4.22	9.22	27.97	31.09	27.19	2.56
146	158.10	6/13/2013	596	88	62	72	84	285	18	14.77	10.40	12.08	14.09	47.82	3.10
147	158.50	6/13/2013	696	83	150	110	86	262	13	11.93	21.55	15.80	12.36	37.64	1.90
148	159.50	6/13/2013	598	118	118	121	92	145	24	19.73	19.73	20.23	15.38	24.25	4.04
149	159.90	6/13/2013	830	79	254	226	114	153	14	9.52	30.60	27.23	13.73	18.43	1.63
150	160.35	6/13/2013	1118	127	146	165	150	527	51	11.36	13.06	14.76	13.42	47.14	4.56
151	160.80	6/13/2013	785	94	142	134	129	279	23	11.97	18.09	17.07	16.43	35.54	2.96
152	161.40	6/13/2013	829	101	164	216	149	204	43	12.18	19.78	26.06	17.97	24.61	5.19
153	162.10	6/13/2013	849	114	124	136	118	358	62	13.43	14.61	16.02	13.90	42.17	7.31
154	162.50	6/13/2013	1015	49	123	311	254	299	36	4.83	12.12	30.64	25.02	29.46	3.56
155	162.50	6/13/2013	975	8	86	369	257	229	34	0.82	8.82	37.85	26.36	23.49	3.50
156	163.00	6/13/2013	858	109	161	181	114	295	40	12.70	18.76	21.10	13.29	34.38	4.65
157	163.35	6/13/2013	715	11	70	216	192	228	37	1.54	9.79	30.21	26.85	31.89	5.19
158	163.70	6/13/2013	1014	23	151	291	225	325	47	2.27	14.89	28.70	22.19	32.05	4.65
159	164.10	6/13/2013	841	140	125	122	85	367	32	16.65	14.86	14.51	10.11	43.64	3.75
160	164.50	6/13/2013	695	173	106	82	59	272	39	24.89	15.25	11.80	8.49	39.14	5.59
161	165.00	6/13/2013	791	144	97	116	117	314	43	18.20	12.26	14.66	14.79	39.70	5.43
162	165.20	6/13/2013	983	38	188	305	252	195	22	3.87	19.13	31.03	25.64	19.84	2.20
163	165.50	6/12/2013	902	53	96	208	208	329	6	5.88	10.64	23.06	23.06	36.47	0.67
164	165.90	6/13/2013	455	23	63	78	66	223	34	5.05	13.85	17.14	14.51	49.01	7.54
165	165.90	6/12/2013	981	99	169	148	104	460	64	10.09	17.23	15.09	10.60	46.89	6.56
166	166.25	6/12/2013	842	184	135	132	101	288	26	21.85	16.03	15.68	12.00	34.20	3.11

Lab #	R-Km/ location	Date	Tot Sample Weight (g)	16-32 mm (g)	8-16 mm (g)	4-8 mm (g)	2-4 mm (g)	<2 mm (g)	<0.25 mm (g)	16-32 mm mass %	8-16 mm mass %	4-8 mm mass %	2-4 mm mass %	<2 mm mass %	<0.25 mm mass %
167	166.40	6/12/2013	605	103	122	101	76	209	12	17.02	20.17	16.69	12.56	34.55	1.94
168	166.90	6/12/2013	805	290	177	145	111	75	15	36.02	21.99	18.01	13.79	9.32	1.86
169	167.00	6/12/2013	717	10	78	112	107	405	11	1.39	10.88	15.62	14.92	56.49	1.52
170	167.00	6/12/2013	580	172	91	130	84	98	18	29.66	15.69	22.41	14.48	16.90	3.05
171	167.20	6/12/2013	894	17	97	238	167	372	9	1.90	10.85	26.62	18.68	41.61	1.02
172	167.50	6/12/2013	923	170	167	180	101	306	12	18.42	18.09	19.50	10.94	33.15	1.30
173	168.10	6/12/2013	765	122	164	185	129	162	9	15.95	21.44	24.18	16.86	21.18	1.18
174	168.10	6/12/2013	407	87	100	47	42	130	12	21.38	24.57	11.55	10.32	31.94	2.85
175	168.80	6/12/2013	396	41	126	125	24	77	23	10.35	31.82	31.57	6.06	19.44	5.74
176	168.85	6/12/2013	794	115	157	131	83	305	18	14.48	19.77	16.50	10.45	38.41	2.33
177	169.15	6/12/2013	810	112	136	149	94	313	11	13.83	16.79	18.40	11.60	38.64	1.39
178	169.20	6/12/2013	555	16	159	133	79	159	10	2.88	28.65	23.96	14.23	28.65	1.88
179	169.80	6/12/2013	494	68	86	66	56	216	38	13.77	17.41	13.36	11.34	43.72	7.75
180	170.00	6/12/2013	564	87	128	90	57	198	9	15.43	22.70	15.96	10.11	35.11	1.53
181	170.05	6/12/2013	652	63	96	135	111	243	10	9.66	14.72	20.71	17.02	37.27	1.52

Appendix D: Sample Lithology Percentages

Lithology percentages for each bar sample were derived from each size fraction. **S**ubsamples of 100-150 grains were randomly picked from each size fraction and sorted into the following classes: dolomite, natural sediment (quartz, chert, etc.) and coal/slag. Separated subsample grains were counted and lithology percentages were calculated by dividing the number of dolomite or natural grains by the total number of grains counted. Although coal and slag sediments originate from smelting operations their occurrence is relatively infrequent and they do not necessarily affect sediment heavy metal concentrations. For this research the coal/slag pieces were added to the Chert/Other category. However, the coal/slag percentage results are available here for reference.

Appendix D-1: Sample Lithology Percentages 2-4 mm

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	**R-Km/ location**	**Dup**	**2-4 mm Chert/ other (#)**	**2-4 mm Dolomite chips (#)**	**2-4 mm Coal/ Slag (#)**	**2-4 mm Total with coal (#)**	**2-4 mm Total w/o coal (#)**	**2-4 mm Chert/ other (%)**	**2-4 mm Dolomite chips (%)**	**2-4 mm Coal/ Slag (%)**	**2-4 mm Chert/ other (%)**	**2-4 mm Dolomite chips (%)**
1	101.87		231	0	3	234	231	98.7	0.0	1.3	100.0	0.0
2	101.75		175	0	3	178	175	98.3	0.0	1.7	100.0	0.0
3	102.45		195	1	15	211	196	92.4	0.5	7.1	99.5	0.5
5	102.90		176	0	23	199	176	88.4	0.0	11.6	100.0	0.0
6	103.40		188	0	13	201	188	93.5	0.0	6.5	100.0	0.0
7	104.15	a	248	0	12	260	248	95.4	0.0	4.6	100.0	0.0
8	104.15	b	215	0	30	245	215	87.8	0.0	12.2	100.0	0.0
9	104.20		179	0	28	207	179	86.5	0.0	13.5	100.0	0.0
10	105.05		220	2	4	226	222	97.3	0.9	1.8	99.1	0.9
11	105.50		178	3	11	192	181	92.7	1.6	5.7	98.3	1.7
12	105.80		203	0	9	212	203	95.8	0.0	4.2	100.0	0.0

Lab #	R-Km/ location	Dup	Counts: 2-4 mm Chert/ other (#)	2-4 mm Dolomite chips (#)	2-4 mm Coal/ Slag (#)	2-4 mm Total with coal (#)	2-4 mm Total w/o coal (#)	Total Percentages with Coal: 2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)	2-4 mm Coal/ Slag (%)	Total Percentages NO coal: 2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)
13	106.20		204	1	9	214	205	95.3	0.5	4.2	99.5	0.5
15	106.50	a	158	4	7	169	162	93.5	2.4	4.1	97.5	2.5
16	106.50	b	287	3	5	295	290	97.3	1.0	1.7	99.0	1.0
17	107.00		169	0	24	193	169	87.6	0.0	12.4	100.0	0.0
18	107.45		166	0	17	183	166	90.7	0.0	9.3	100.0	0.0
19	107.80		144	0	0	144	144	100.0	0.0	0.0	100.0	0.0
21	108.25		210	0	1	211	210	99.5	0.0	0.5	100.0	0.0
23	108.60	a	200	0	1	201	200	99.5	0.0	0.5	100.0	0.0
24	108.60	b	256	1	2	259	257	98.8	0.4	0.8	99.6	0.4
25	109.60		156	2	9	167	158	93.4	1.2	5.4	98.7	1.3
26	109.75		182	0	13	195	182	93.3	0.0	6.7	100.0	0.0
27	110.80		254	0	0	254	254	100.0	0.0	0.0	100.0	0.0
28	111.45	a	184	0	25	209	184	88.0	0.0	12.0	100.0	0.0
29	111.45	b	165	0	12	177	165	93.2	0.0	6.8	100.0	0.0
30	111.50		164	2	11	177	166	92.7	1.1	6.2	98.8	1.2
31	111.75		364	3	6	373	367	97.6	0.8	1.6	99.2	0.8
32	112.10		256	2	12	270	258	94.8	0.7	4.4	99.2	0.8
34	112.60	b	167	1	6	174	168	96.0	0.6	3.4	99.4	0.6
35	112.60	a	259	0	4	263	259	98.5	0.0	1.5	100.0	0.0
36	113.00		244	3	4	251	247	97.2	1.2	1.6	98.8	1.2
37	113.50	a	205	3	22	230	208	89.1	1.3	9.6	98.6	1.4
38	113.50	b	233	4	16	253	237	92.1	1.6	6.3	98.3	1.7
39	115.00		188	4	23	215	192	87.4	1.9	10.7	97.9	2.1
40	115.40		242	1	1	244	243	99.2	0.4	0.4	99.6	0.4
41	115.80		245	4	11	260	249	94.2	1.5	4.2	98.4	1.6
42	116.30		317	7	57	381	324	83.2	1.8	15.0	97.8	2.2
44	116.60	a	230	7	14	251	237	91.6	2.8	5.6	97.0	3.0
45	116.60	b	227	3	49	279	230	81.4	1.1	17.6	98.7	1.3
46	117.50		220	13	18	251	233	87.6	5.2	7.2	94.4	5.6
47	117.80		216	5	7	228	221	94.7	2.2	3.1	97.7	2.3

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	2-4 mm Chert/ other (#)	2-4 mm Dolomite chips (#)	2-4 mm Coal/ Slag (#)	2-4 mm Total with coal (#)	2-4 mm Total w/o coal (#)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)	2-4 mm Coal/ Slag (%)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)
48	118.15		243	22	11	276	265	88.0	8.0	4.0	91.7	8.3
49	118.60	a	187	9	12	208	196	89.9	4.3	5.8	95.4	4.6
50	118.60	b	198	12	49	259	210	76.4	4.6	18.9	94.3	5.7
52	118.90		250	8	16	274	258	91.2	2.9	5.8	96.9	3.1
53	119.40		153	1	12	166	154	92.2	0.6	7.2	99.4	0.6
54	120.20		280	16	29	325	296	86.2	4.9	8.9	94.6	5.4
55	120.60	a	229	13	53	295	242	77.6	4.4	18.0	94.6	5.4
56	120.60	b	228	8	10	246	236	92.7	3.3	4.1	96.6	3.4
57	121.05		223	9	25	257	232	86.8	3.5	9.7	96.1	3.9
58	121.45	a	168	21	4	193	189	87.0	10.9	2.1	88.9	11.1
59	121.45	b	138	13	3	154	151	89.6	8.4	1.9	91.4	8.6
60	121.50		181	11	6	198	192	91.4	5.6	3.0	94.3	5.7
62	122.00		145	9	16	170	154	85.3	5.3	9.4	94.2	5.8
63	123.20		208	20	12	240	228	86.7	8.3	5.0	91.2	8.8
64	123.55		136	7	3	146	143	93.2	4.8	2.1	95.1	4.9
65	124.20		200	20	25	245	220	81.6	8.2	10.2	90.9	9.1
66	124.60	a	143	24	10	177	167	80.8	13.6	5.6	85.6	14.4
67	124.60	b	192	29	20	241	221	79.7	12.0	8.3	86.9	13.1
68	125.05		159	26	7	192	185	82.8	13.5	3.6	85.9	14.1
69	125.40		170	13	8	191	183	89.0	6.8	4.2	92.9	7.1
70	126.05		125	35	2	162	160	77.2	21.6	1.2	78.1	21.9
71	126.50	a	230	31	11	272	261	84.6	11.4	4.0	88.1	11.9
72	126.50	b	232	40	11	283	272	82.0	14.1	3.9	85.3	14.7
74	127.00		185	19	7	211	204	87.7	9.0	3.3	90.7	9.3
75	127.30		163	20	20	203	183	80.3	9.9	9.9	89.1	10.9
76	127.85		189	15	12	216	204	87.5	6.9	5.6	92.6	7.4
77	128.15		158	17	18	193	175	81.9	8.8	9.3	90.3	9.7
78	128.65	a	158	32	12	202	190	78.2	15.8	5.9	83.2	16.8
79	128.65	b	143	36	7	186	179	76.9	19.4	3.8	79.9	20.1
80	128.95		139	9	1	149	148	93.3	6.0	0.7	93.9	6.1

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	2-4 mm Chert/ other (#)	2-4 mm Dolomite chips (#)	2-4 mm Coal/ Slag (#)	2-4 mm Total with coal (#)	2-4 mm Total w/o coal (#)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)	2-4 mm Coal/ Slag (%)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)
81	129.40		288	89	11	388	377	74.2	22.9	2.8	76.4	23.6
82	130.10		80	27	40	147	107	54.4	18.4	27.2	74.8	25.2
83	130.30	a	52	19	33	104	71	50.0	18.3	31.7	73.2	26.8
84	130.30	b	134	99	8	241	233	55.6	41.1	3.3	57.5	42.5
85	130.85		142	43	16	201	185	70.6	21.4	8.0	76.8	23.2
86	131.00		126	48	14	188	174	67.0	25.5	7.4	72.4	27.6
87	131.40	a	130	102	10	242	232	53.7	42.1	4.1	56.0	44.0
88	131.40	b	145	104	9	258	249	56.2	40.3	3.5	58.2	41.8
89	132.20		98	26	50	174	124	56.3	14.9	28.7	79.0	21.0
90	132.65	b	173	133	14	320	306	54.1	41.6	4.4	56.5	43.5
91	132.65	a	80	82	9	171	162	46.8	48.0	5.3	49.4	50.6
92	132.90		214	89	88	391	303	54.7	22.8	22.5	70.6	29.4
93	133.30		238	99	10	347	337	68.6	28.5	2.9	70.6	29.4
94	133.70		342	181	29	552	523	62.0	32.8	5.3	65.4	34.6
95	134.00		40	46	9	95	86	42.1	48.4	9.5	46.5	53.5
96	134.50		36	57	4	97	93	37.1	58.8	4.1	38.7	61.3
97	135.00		197	146	24	367	343	53.7	39.8	6.5	57.4	42.6
98	135.50		66	46	11	123	112	53.7	37.4	8.9	58.9	41.1
99	136.00		82	101	16	199	183	41.2	50.8	8.0	44.8	55.2
100	136.30		93	66	19	178	159	52.2	37.1	10.7	58.5	41.5
101	136.90		32	113	7	152	145	21.1	74.3	4.6	22.1	77.9
102	137.40		87	94	14	195	181	44.6	48.2	7.2	48.1	51.9
103	138.00		60	92	15	167	152	35.9	55.1	9.0	39.5	60.5
104	138.50		77	77	16	170	154	45.3	45.3	9.4	50.0	50.0
105	139.00		42	97	8	147	139	28.6	66.0	5.4	30.2	69.8
106	139.50		54	77	13	144	131	37.5	53.5	9.0	41.2	58.8
107	140.00	a	64	96	25	185	160	34.6	51.9	13.5	40.0	60.0
108	140.00	b	42	72	7	121	114	34.7	59.5	5.8	36.8	63.2
109	140.80		46	48	8	102	94	45.1	47.1	7.8	48.9	51.1
110	141.50		34	80	10	124	114	27.4	64.5	8.1	29.8	70.2

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	2-4 mm Chert/ other (#)	2-4 mm Dolomite chips (#)	2-4 mm Coal/ Slag (#)	2-4 mm Total with coal (#)	2-4 mm Total w/o coal (#)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)	2-4 mm Coal/ Slag (%)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)
111	141.85		59	49	18	126	108	46.8	38.9	14.3	54.6	45.4
112	142.30		63	83	26	172	146	36.6	48.3	15.1	43.2	56.8
113	142.80		49	75	6	130	124	37.7	57.7	4.6	39.5	60.5
114	143.20		47	80	4	131	127	35.9	61.1	3.1	37.0	63.0
115	143.70		56	55	16	127	111	44.1	43.3	12.6	50.5	49.5
116	144.10		64	80	10	154	144	41.6	51.9	6.5	44.4	55.6
117	144.50		234	225	48	507	459	46.2	44.4	9.5	51.0	49.0
118	145.00	a	44	87	1	132	131	33.3	65.9	0.8	33.6	66.4
119	145.00	b	38	66	4	108	104	35.2	61.1	3.7	36.5	63.5
120	145.40		44	74	8	126	118	34.9	58.7	6.3	37.3	62.7
121	145.90		38	100	6	144	138	26.4	69.4	4.2	27.5	72.5
122	146.30		29	68	4	101	97	28.7	67.3	4.0	29.9	70.1
123	146.70		55	47	10	112	102	49.1	42.0	8.9	53.9	46.1
124	147.00	a	114	52	13	179	166	63.7	29.1	7.3	68.7	31.3
125	147.00	b	84	57	7	148	141	56.8	38.5	4.7	59.6	40.4
126	147.40		60	45	10	115	105	52.2	39.1	8.7	57.1	42.9
127	148.05		178	199	14	391	377	45.5	50.9	3.6	47.2	52.8
128	148.50		39	28	16	83	67	47.0	33.7	19.3	58.2	41.8
129	148.90		44	52	3	99	96	44.4	52.5	3.0	45.8	54.2
130	149.80		43	39	5	87	82	49.4	44.8	5.7	52.4	47.6
131	150.20		27	92	6	125	119	21.6	73.6	4.8	22.7	77.3
132	150.70		57	92	7	156	149	36.5	59.0	4.5	38.3	61.7
133	151.70		76	59	6	141	135	53.9	41.8	4.3	56.3	43.7
134	152.40		64	42	8	114	106	56.1	36.8	7.0	60.4	39.6
135	152.80		79	63	11	153	142	51.6	41.2	7.2	55.6	44.4
136	153.30		72	49	6	127	121	56.7	38.6	4.7	59.5	40.5
137	153.40		31	106	2	139	137	22.3	76.3	1.4	22.6	77.4
138	153.70		87	88	3	178	175	48.9	49.4	1.7	49.7	50.3
139	154.70		69	40	7	116	109	59.5	34.5	6.0	63.3	36.7
140	155.10		27	103	1	131	130	20.6	78.6	0.8	20.8	79.2

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	2-4 mm Chert/ other (#)	2-4 mm Dolomite chips (#)	2-4 mm Coal/ Slag (#)	2-4 mm Total with coal (#)	2-4 mm Total w/o coal (#)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)	2-4 mm Coal/ Slag (%)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)
141	155.60		58	43	13	114	101	50.9	37.7	11.4	57.4	42.6
142	156.00		67	49	9	125	116	53.6	39.2	7.2	57.8	42.2
143	156.80		38	55	6	99	93	38.4	55.6	6.1	40.9	59.1
144	157.60		47	22	15	84	69	56.0	26.2	17.9	68.1	31.9
145	158.00		49	74	2	125	123	39.2	59.2	1.6	39.8	60.2
146	158.10		51	64	4	119	115	42.9	53.8	3.4	44.3	55.7
147	158.50		108	151	19	278	259	38.8	54.3	6.8	41.7	58.3
148	159.50		63	38	3	104	101	60.6	36.5	2.9	62.4	37.6
149	159.90		60	51	6	117	111	51.3	43.6	5.1	54.1	45.9
150	160.35		46	48	4	98	94	46.9	49.0	4.1	48.9	51.1
151	160.80		53	96	10	159	149	33.3	60.4	6.3	35.6	64.4
152	161.40		53	82	2	137	135	38.7	59.9	1.5	39.3	60.7
153	162.10		62	75	5	142	137	43.7	52.8	3.5	45.3	54.7
154	162.50	a	43	50	2	95	93	45.3	52.6	2.1	46.2	53.8
155	162.50	b	50	38	0	88	88	56.8	43.2	0.0	56.8	43.2
156	163.00		47	35	5	87	82	54.0	40.2	5.7	57.3	42.7
157	163.35		67	45	5	117	112	57.3	38.5	4.3	59.8	40.2
158	163.70		61	32	1	94	93	64.9	34.0	1.1	65.6	34.4
159	164.10		55	54	6	115	109	47.8	47.0	5.2	50.5	49.5
160	164.50		44	47	8	99	91	44.4	47.5	8.1	48.4	51.6
161	165.00		32	44	4	80	76	40.0	55.0	5.0	42.1	57.9
162	165.20		79	47	2	128	126	61.7	36.7	1.6	62.7	37.3
163	165.50		57	33	1	91	90	62.6	36.3	1.1	63.3	36.7
164	165.90	a	77	62	6	145	139	53.1	42.8	4.1	55.4	44.6
165	165.90	b	65	39	11	115	104	56.5	33.9	9.6	62.5	37.5
166	166.25		68	59	3	130	127	52.3	45.4	2.3	53.5	46.5
167	166.40		115	80	19	214	195	53.7	37.4	8.9	59.0	41.0
168	166.90		79	42	12	133	121	59.4	31.6	9.0	65.3	34.7
169	167.00	a	80	11	5	96	91	83.3	11.5	5.2	87.9	12.1
170	167.00	b	60	51	3	114	111	52.6	44.7	2.6	54.1	45.9

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	2-4 mm Chert/ other (#)	2-4 mm Dolomite chips (#)	2-4 mm Coal/ Slag (#)	2-4 mm Total with coal (#)	2-4 mm Total w/o coal (#)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)	2-4 mm Coal/ Slag (%)	2-4 mm Chert/ other (%)	2-4 mm Dolomite chips (%)
171	167.20		102	15	0	117	117	87.2	12.8	0.0	87.2	12.8
172	167.50		109	28	4	141	137	77.3	19.9	2.8	79.6	20.4
173	168.10	a	94	17	4	115	111	81.7	14.8	3.5	84.7	15.3
174	168.10	b	87	21	5	113	108	77.0	18.6	4.4	80.6	19.4
175	168.80		118	14	7	139	132	84.9	10.1	5.0	89.4	10.6
176	168.85		98	18	12	128	116	76.6	14.1	9.4	84.5	15.5
177	169.15		134	22	8	164	156	81.7	13.4	4.9	85.9	14.1
178	169.20		154	24	5	183	178	84.2	13.1	2.7	86.5	13.5
179	169.80		107	14	3	124	121	86.3	11.3	2.4	88.4	11.6
180	170.00		111	9	6	126	120	88.1	7.1	4.8	92.5	7.5
181	170.05		287	10	6	303	297	94.7	3.3	2.0	96.6	3.4

Appendix D-2: Sample Lithology Percentages 4-8 mm

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	4-8 mm Chert/ other (#)	4-8 mm Dolomite chips (#)	4-8 mm Coal/ Slag (#)	4-8 mm Total with coal (#)	4-8 mm Total w/o coal (#)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)	4-8 mm Coal/ Slag (%)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)
1	101.87		67	0	1	68	67	98.5	0.0	1.5	100.0	0.0
2	101.75		92	0	3	95	92	96.8	0.0	3.2	100.0	0.0
3	102.45		72	0	19	91	72	79.1	0.0	20.9	100.0	0.0
5	102.90		52	0	6	58	52	89.7	0.0	10.3	100.0	0.0
6	103.40		57	1	5	63	58	90.5	1.6	7.9	98.3	1.7
7	104.15	a	106	0	2	108	106	98.1	0.0	1.9	100.0	0.0
8	104.15	b	58	0	17	75	58	77.3	0.0	22.7	100.0	0.0
9	104.20		67	0	43	110	67	60.9	0.0	39.1	100.0	0.0
10	105.05		108	1	2	111	109	97.3	0.9	1.8	99.1	0.9
11	105.50		41	1	6	48	42	85.4	2.1	12.5	97.6	2.4
12	105.80		83	0	4	87	83	95.4	0.0	4.6	100.0	0.0
13	106.20		94	0	3	97	94	96.9	0.0	3.1	100.0	0.0
15	106.50	a	72	0	4	76	72	94.7	0.0	5.3	100.0	0.0
16	106.50	b	86	0	2	88	86	97.7	0.0	2.3	100.0	0.0
17	107.00		75	0	20	95	75	78.9	0.0	21.1	100.0	0.0
18	107.45		69	0	6	75	69	92.0	0.0	8.0	100.0	0.0
19	107.80		114	0	0	114	114	100.0	0.0	0.0	100.0	0.0
21	108.25		65	0	0	65	65	100.0	0.0	0.0	100.0	0.0
23	108.60	a	104	0	0	104	104	100.0	0.0	0.0	100.0	0.0
24	108.60	b	85	0	1	86	85	98.8	0.0	1.2	100.0	0.0
25	109.60		99	1	7	107	100	92.5	0.9	6.5	99.0	1.0
26	109.75		62	0	2	64	62	96.9	0.0	3.1	100.0	0.0
27	110.80		77	3	1	81	80	95.1	3.7	1.2	96.3	3.8
28	111.45	a	66	0	3	69	66	95.7	0.0	4.3	100.0	0.0
29	111.45	b	68	0	5	73	68	93.2	0.0	6.8	100.0	0.0
30	111.50		100	0	17	117	100	85.5	0.0	14.5	100.0	0.0
31	111.75		101	0	3	104	101	97.1	0.0	2.9	100.0	0.0
32	112.10		84	0	4	88	84	95.5	0.0	4.5	100.0	0.0

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	4-8 mm Chert/ other (#)	4-8 mm Dolomite chips (#)	4-8 mm Coal/ Slag (#)	4-8 mm Total with coal (#)	4-8 mm Total w/o coal (#)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)	4-8 mm Coal/ Slag (%)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)
34	112.60	b	89	0	1	90	89	98.9	0.0	1.1	100.0	0.0
35	112.60	a	68	0	1	69	68	98.6	0.0	1.4	100.0	0.0
36	113.00		43	1	4	48	44	89.6	2.1	8.3	97.7	2.3
37	113.50	a	79	0	18	97	79	81.4	0.0	18.6	100.0	0.0
38	113.50	b	67	0	9	76	67	88.2	0.0	11.8	100.0	0.0
39	115.00		81	0	23	104	81	77.9	0.0	22.1	100.0	0.0
40	115.40		76	0	2	78	76	97.4	0.0	2.6	100.0	0.0
41	115.80		121	0	7	128	121	94.5	0.0	5.5	100.0	0.0
42	116.30		90	2	15	107	92	84.1	1.9	14.0	97.8	2.2
44	116.60	a	50	0	9	59	50	84.7	0.0	15.3	100.0	0.0
45	116.60	b	61	0	56	117	61	52.1	0.0	47.9	100.0	0.0
46	117.50		111	0	17	128	111	86.7	0.0	13.3	100.0	0.0
47	117.80		105	0	4	109	105	96.3	0.0	3.7	100.0	0.0
48	118.15		80	0	24	104	80	76.9	0.0	23.1	100.0	0.0
49	118.60	a	80	2	11	93	82	86.0	2.2	11.8	97.6	2.4
50	118.60	b	117	1	17	135	118	86.7	0.7	12.6	99.2	0.8
52	118.90		93	1	7	101	94	92.1	1.0	6.9	98.9	1.1
53	119.40		92	0	2	94	92	97.9	0.0	2.1	100.0	0.0
54	120.20		92	1	15	108	93	85.2	0.9	13.9	98.9	1.1
55	120.60	a	71	1	23	95	72	74.7	1.1	24.2	98.6	1.4
56	120.60	b	88	0	2	90	88	97.8	0.0	2.2	100.0	0.0
57	121.05		91	0	19	110	91	82.7	0.0	17.3	100.0	0.0
58	121.45	a	104	3	2	109	107	95.4	2.8	1.8	97.2	2.8
59	121.45	b	101	4	0	105	105	96.2	3.8	0.0	96.2	3.8
60	121.50		98	2	5	105	100	93.3	1.9	4.8	98.0	2.0
62	122.00		87	1	10	98	88	88.8	1.0	10.2	98.9	1.1
63	123.20		101	2	5	108	103	93.5	1.9	4.6	98.1	1.9
64	123.55		81	2	2	85	83	95.3	2.4	2.4	97.6	2.4
65	124.20		80	4	3	87	84	92.0	4.6	3.4	95.2	4.8
66	124.60	a	88	6	6	100	94	88.0	6.0	6.0	93.6	6.4

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	4-8 mm Chert/ other (#)	4-8 mm Dolomite chips (#)	4-8 mm Coal/ Slag (#)	4-8 mm Total with coal (#)	4-8 mm Total w/o coal (#)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)	4-8 mm Coal/ Slag (%)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)
67	124.60	b	92	9	11	112	101	82.1	8.0	9.8	91.1	8.9
68	125.05		79	2	0	81	81	97.5	2.5	0.0	97.5	2.5
69	125.40		105	2	4	111	107	94.6	1.8	3.6	98.1	1.9
70	126.05		74	6	2	82	80	90.2	7.3	2.4	92.5	7.5
71	126.50	a	88	4	2	94	92	93.6	4.3	2.1	95.7	4.3
72	126.50	b	105	3	5	113	108	92.9	2.7	4.4	97.2	2.8
74	127.00		80	2	3	85	82	94.1	2.4	3.5	97.6	2.4
75	127.30		90	6	6	102	96	88.2	5.9	5.9	93.8	6.3
76	127.85		77	4	7	88	81	87.5	4.5	8.0	95.1	4.9
77	128.15		77	3	10	90	80	85.6	3.3	11.1	96.3	3.8
78	128.65	a	58	5	13	76	63	76.3	6.6	17.1	92.1	7.9
79	128.65	b	104	4	11	119	108	87.4	3.4	9.2	96.3	3.7
80	128.95		100	2	0	102	102	98.0	2.0	0.0	98.0	2.0
81	129.40		77	9	3	89	86	86.5	10.1	3.4	89.5	10.5
82	130.10		26	5	32	63	31	41.3	7.9	50.8	83.9	16.1
83	130.30	a	44	6	35	85	50	51.8	7.1	41.2	88.0	12.0
84	130.30	b	73	8	2	83	81	88.0	9.6	2.4	90.1	9.9
85	130.85		84	6	1	91	90	92.3	6.6	1.1	93.3	6.7
86	131.00		96	8	9	113	104	85.0	7.1	8.0	92.3	7.7
87	131.40	a	74	18	0	92	92	80.4	19.6	0.0	80.4	19.6
88	131.40	b	90	11	1	102	101	88.2	10.8	1.0	89.1	10.9
89	132.20		66	6	39	111	72	59.5	5.4	35.1	91.7	8.3
90	132.65	b	76	22	1	99	98	76.8	22.2	1.0	77.6	22.4
91	132.65	a	76	21	0	97	97	78.4	21.6	0.0	78.4	21.6
92	132.90		103	7	13	123	110	83.7	5.7	10.6	93.6	6.4
93	133.30		52	5	7	64	57	81.3	7.8	10.9	91.2	8.8
94	133.70		52	4	2	58	56	89.7	6.9	3.4	92.9	7.1
95	134.00		62	17	11	90	79	68.9	18.9	12.2	78.5	21.5
96	134.50		53	23	4	80	76	66.3	28.8	5.0	69.7	30.3
97	135.00		70	17	7	94	87	74.5	18.1	7.4	80.5	19.5

Lab #	R-Km/ location	Dup	Counts: 4-8 mm Chert/ other (#)	4-8 mm Dolomite chips (#)	4-8 mm Coal/ Slag (#)	4-8 mm Total with coal (#)	4-8 mm Total w/o coal (#)	Total Percentages with Coal: 4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)	4-8 mm Coal/ Slag (%)	Total Percentages NO coal: 4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)
98	135.50		74	28	7	109	102	67.9	25.7	6.4	72.5	27.5
99	136.00		50	17	6	73	67	68.5	23.3	8.2	74.6	25.4
100	136.30		45	28	14	87	73	51.7	32.2	16.1	61.6	38.4
101	136.90		60	49	0	109	109	55.0	45.0	0.0	55.0	45.0
102	137.40		67	33	8	108	100	62.0	30.6	7.4	67.0	33.0
103	138.00		66	36	9	111	102	59.5	32.4	8.1	64.7	35.3
104	138.50		61	55	6	122	116	50.0	45.1	4.9	52.6	47.4
105	139.00		68	54	2	124	122	54.8	43.5	1.6	55.7	44.3
106	139.50		63	48	7	118	111	53.4	40.7	5.9	56.8	43.2
107	140.00	a	41	17	13	71	58	57.7	23.9	18.3	70.7	29.3
108	140.00	b	50	40	7	97	90	51.5	41.2	7.2	55.6	44.4
109	140.80		47	25	10	82	72	57.3	30.5	12.2	65.3	34.7
110	141.50		41	41	2	84	82	48.8	48.8	2.4	50.0	50.0
111	141.85		34	23	16	73	57	46.6	31.5	21.9	59.6	40.4
112	142.30		47	31	17	95	78	49.5	32.6	17.9	60.3	39.7
113	142.80		48	52	14	114	100	42.1	45.6	12.3	48.0	52.0
114	143.20		67	60	6	133	127	50.4	45.1	4.5	52.8	47.2
115	143.70		56	28	17	101	84	55.4	27.7	16.8	66.7	33.3
116	144.10		46	27	23	96	73	47.9	28.1	24.0	63.0	37.0
117	144.50		46	33	6	85	79	54.1	38.8	7.1	58.2	41.8
118	145.00	a	49	67	0	116	116	42.2	57.8	0.0	42.2	57.8
119	145.00	b	52	71	4	127	123	40.9	55.9	3.1	42.3	57.7
120	145.40		77	61	1	139	138	55.4	43.9	0.7	55.8	44.2
121	145.90		59	73	1	133	132	44.4	54.9	0.8	44.7	55.3
122	146.30		51	84	2	137	135	37.2	61.3	1.5	37.8	62.2
123	146.70		83	38	5	126	121	65.9	30.2	4.0	68.6	31.4
124	147.00	a	83	12	5	100	95	83.0	12.0	5.0	87.4	12.6
125	147.00	b	105	18	10	133	123	78.9	13.5	7.5	85.4	14.6
126	147.40		62	21	29	112	83	55.4	18.8	25.9	74.7	25.3
127	148.05		62	52	2	116	114	53.4	44.8	1.7	54.4	45.6

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	4-8 mm Chert/ other (#)	4-8 mm Dolomite chips (#)	4-8 mm Coal/ Slag (#)	4-8 mm Total with coal (#)	4-8 mm Total w/o coal (#)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)	4-8 mm Coal/ Slag (%)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)
128	148.50		87	24	17	128	111	68.0	18.8	13.3	78.4	21.6
129	148.90		74	44	2	120	118	61.7	36.7	1.7	62.7	37.3
130	149.80		58	69	4	131	127	44.3	52.7	3.1	45.7	54.3
131	150.20		59	92	3	154	151	38.3	59.7	1.9	39.1	60.9
132	150.70		66	27	12	105	93	62.9	25.7	11.4	71.0	29.0
133	151.70		81	30	11	122	111	66.4	24.6	9.0	73.0	27.0
134	152.40		55	48	9	112	103	49.1	42.9	8.0	53.4	46.6
135	152.80		47	24	4	75	71	62.7	32.0	5.3	66.2	33.8
136	153.30		68	22	17	107	90	63.6	20.6	15.9	75.6	24.4
137	153.40		52	50	1	103	102	50.5	48.5	1.0	51.0	49.0
138	153.70		51	49	1	101	100	50.5	48.5	1.0	51.0	49.0
139	154.70		84	18	7	109	102	77.1	16.5	6.4	82.4	17.6
140	155.10		59	113	9	181	172	32.6	62.4	5.0	34.3	65.7
141	155.60		58	27	34	119	85	48.7	22.7	28.6	68.2	31.8
142	156.00		103	59	11	173	162	59.5	34.1	6.4	63.6	36.4
143	156.80		74	27	3	104	101	71.2	26.0	2.9	73.3	26.7
144	157.60		87	24	18	129	111	67.4	18.6	14.0	78.4	21.6
145	158.00		83	46	2	131	129	63.4	35.1	1.5	64.3	35.7
146	158.10		55	61	11	127	116	43.3	48.0	8.7	47.4	52.6
147	158.50		61	73	7	141	134	43.3	51.8	5.0	45.5	54.5
148	159.50		96	40	4	140	136	68.6	28.6	2.9	70.6	29.4
149	159.90		88	46	8	142	134	62.0	32.4	5.6	65.7	34.3
150	160.35		83	56	11	150	139	55.3	37.3	7.3	59.7	40.3
151	160.80		98	61	19	178	159	55.1	34.3	10.7	61.6	38.4
152	161.40		84	80	1	165	164	50.9	48.5	0.6	51.2	48.8
153	162.10		72	44	1	117	116	61.5	37.6	0.9	62.1	37.9
154	162.50	a	115	75	2	192	190	59.9	39.1	1.0	60.5	39.5
155	162.50	b	69	44	1	114	113	60.5	38.6	0.9	61.1	38.9
156	163.00		77	43	9	129	120	59.7	33.3	7.0	64.2	35.8
157	163.35		100	44	3	147	144	68.0	29.9	2.0	69.4	30.6

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	4-8 mm Chert/ other (#)	4-8 mm Dolomite chips (#)	4-8 mm Coal/ Slag (#)	4-8 mm Total with coal (#)	4-8 mm Total w/o coal (#)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)	4-8 mm Coal/ Slag (%)	4-8 mm Chert/ other (%)	4-8 mm Dolomite chips (%)
158	163.70		127	43	5	175	170	72.6	24.6	2.9	74.7	25.3
159	164.10		76	75	5	156	151	48.7	48.1	3.2	50.3	49.7
160	164.50		75	24	8	107	99	70.1	22.4	7.5	75.8	24.2
161	165.00		88	42	10	140	130	62.9	30.0	7.1	67.7	32.3
162	165.20		124	45	0	169	169	73.4	26.6	0.0	73.4	26.6
163	165.50		75	23	3	101	98	74.3	22.8	3.0	76.5	23.5
164	165.90	a	70	42	4	116	112	60.3	36.2	3.4	62.5	37.5
165	165.90	b	84	25	3	112	109	75.0	22.3	2.7	77.1	22.9
166	166.25		55	29	1	85	84	64.7	34.1	1.2	65.5	34.5
167	166.40		56	12	14	82	68	68.3	14.6	17.1	82.4	17.6
168	166.90		66	21	1	88	87	75.0	23.9	1.1	75.9	24.1
169	167.00	a	81	9	2	92	90	88.0	9.8	2.2	90.0	10.0
170	167.00	b	68	20	2	90	88	75.6	22.2	2.2	77.3	22.7
171	167.20		114	11	1	126	125	90.5	8.7	0.8	91.2	8.8
172	167.50		85	17	2	104	102	81.7	16.3	1.9	83.3	16.7
173	168.10	a	97	16	2	115	113	84.3	13.9	1.7	85.8	14.2
174	168.10	b	80	25	9	114	105	70.2	21.9	7.9	76.2	23.8
175	168.80		62	14	3	79	76	78.5	17.7	3.8	81.6	18.4
176	168.85		71	12	5	88	83	80.7	13.6	5.7	85.5	14.5
177	169.15		99	11	3	113	110	87.6	9.7	2.7	90.0	10.0
178	169.20		135	29	2	166	164	81.3	17.5	1.2	82.3	17.7
179	169.80		95	8	0	103	103	92.2	7.8	0.0	92.2	7.8
180	170.00		103	3	3	109	106	94.5	2.8	2.8	97.2	2.8
181	170.05		101	3	4	108	104	93.5	2.8	3.7	97.1	2.9

Appendix D-3: Sample Lithology Percentages 8-16 mm

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	8-16 mm Chert/ other (#)	8-16 mm Dolomite chips (#)	8-16 mm Coal/ Slag (#)	8-16 mm Total with coal (#)	8-16 mm Total w/o coal (#)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)	8-16 mm Coal/ Slag (%)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)
1	101.87		121	0	2	123	121	98.4	0.0	1.6	100.0	0.0
2	101.75		106	0	0	106	106	100.0	0.0	0.0	100.0	0.0
3	102.45		51	0	8	59	51	86.4	0.0	13.6	100.0	0.0
5	102.90		60	0	3	63	60	95.2	0.0	4.8	100.0	0.0
6	103.40		90	0	4	94	90	95.7	0.0	4.3	100.0	0.0
7	104.15	a	82	1	0	83	83	98.8	1.2	0.0	98.8	1.2
8	104.15	b	97	0	6	103	97	94.2	0.0	5.8	100.0	0.0
9	104.20		37	0	25	62	37	59.7	0.0	40.3	100.0	0.0
10	105.05		98	0	3	101	98	97.0	0.0	3.0	100.0	0.0
11	105.50		116	0	18	134	116	86.6	0.0	13.4	100.0	0.0
12	105.80		47	0	1	48	47	97.9	0.0	2.1	100.0	0.0
13	106.20		91	0	0	91	91	100.0	0.0	0.0	100.0	0.0
15	106.50	a	76	0	4	80	76	95.0	0.0	5.0	100.0	0.0
16	106.50	b	115	0	1	116	115	99.1	0.0	0.9	100.0	0.0
17	107.00		104	0	10	114	104	91.2	0.0	8.8	100.0	0.0
18	107.45		104	0	2	106	104	98.1	0.0	1.9	100.0	0.0
19	107.80		99	1	2	102	100	97.1	1.0	2.0	99.0	1.0
21	108.25		159	0	0	159	159	100.0	0.0	0.0	100.0	0.0
23	108.60	a	123	1	1	125	124	98.4	0.8	0.8	99.2	0.8
24	108.60	b	83	0	0	83	83	100.0	0.0	0.0	100.0	0.0
25	109.60		49	0	0	49	49	100.0	0.0	0.0	100.0	0.0
26	109.75		129	1	3	133	130	97.0	0.8	2.3	99.2	0.8
27	110.80		133	3	1	137	136	97.1	2.2	0.7	97.8	2.2
28	111.45	a	137	1	6	144	138	95.1	0.7	4.2	99.3	0.7
29	111.45	b	69	1	3	73	70	94.5	1.4	4.1	98.6	1.4

			Counts						Total Percentages with Coal		Total Percentages NO coal	
Lab #	R-Km/ location	Dup	8-16 mm Chert/ other (#)	8-16 mm Dolomite chips (#)	8-16 mm Coal/ Slag (#)	8-16 mm Total with coal (#)	8-16 mm Total w/o coal (#)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)	8-16 mm Coal/ Slag (%)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)
30	111.50		48	0	5	53	48	90.6	0.0	9.4	100.0	0.0
31	111.75		87	0	1	88	87	98.9	0.0	1.1	100.0	0.0
32	112.10		72	0	0	72	72	100.0	0.0	0.0	100.0	0.0
34	112.60	b	97	0	1	98	97	99.0	0.0	1.0	100.0	0.0
35	112.60	a	85	0	0	85	85	100.0	0.0	0.0	100.0	0.0
36	113.00		118	0	0	118	118	100.0	0.0	0.0	100.0	0.0
37	113.50	a	19	0	1	20	19	95.0	0.0	5.0	100.0	0.0
38	113.50	b	72	0	2	74	72	97.3	0.0	2.7	100.0	0.0
39	115.00		84	0	7	91	84	92.3	0.0	7.7	100.0	0.0
40	115.40		73	0	0	73	73	100.0	0.0	0.0	100.0	0.0
41	115.80		93	0	1	94	93	98.9	0.0	1.1	100.0	0.0
42	116.30		98	0	3	101	98	97.0	0.0	3.0	100.0	0.0
44	116.60	a	92	0	6	98	92	93.9	0.0	6.1	100.0	0.0
45	116.60	b	49	0	30	79	49	62.0	0.0	38.0	100.0	0.0
46	117.50		47	0	2	49	47	95.9	0.0	4.1	100.0	0.0
47	117.80		4	0	0	4	4	100.0	0.0	0.0	100.0	0.0
48	118.15		17	0	2	19	17	89.5	0.0	10.5	100.0	0.0
49	118.60	a	52	0	7	59	52	88.1	0.0	11.9	100.0	0.0
50	118.60	b	61	0	7	68	61	89.7	0.0	10.3	100.0	0.0
52	118.90		51	0	3	54	51	94.4	0.0	5.6	100.0	0.0
53	119.40		25	0	0	25	25	100.0	0.0	0.0	100.0	0.0
54	120.20		65	0	5	70	65	92.9	0.0	7.1	100.0	0.0
55	120.60	a	79	0	4	83	79	95.2	0.0	4.8	100.0	0.0
56	120.60	b	152	0	4	156	152	97.4	0.0	2.6	100.0	0.0
57	121.05		47	0	0	47	47	100.0	0.0	0.0	100.0	0.0
58	121.45	a	68	0	0	68	68	100.0	0.0	0.0	100.0	0.0
59	121.45	b	87	0	0	87	87	100.0	0.0	0.0	100.0	0.0
60	121.50		43	0	0	43	43	100.0	0.0	0.0	100.0	0.0
62	122.00		78	0	13	91	78	85.7	0.0	14.3	100.0	0.0

Lab #	R-Km/ location	Dup	Counts: 8-16 mm Chert/ other (#)	Counts: 8-16 mm Dolomite chips (#)	Counts: 8-16 mm Coal/ Slag (#)	Counts: 8-16 mm Total with coal (#)	Counts: 8-16 mm Total w/o coal (#)	Total Percentages with Coal: 8-16 mm Chert/ other (%)	Total Percentages with Coal: 8-16 mm Dolomite chips (%)	Total Percentages with Coal: 8-16 mm Coal/ Slag (%)	Total Percentages NO coal: 8-16 mm Chert/ other (%)	Total Percentages NO coal: 8-16 mm Dolomite chips (%)
63	123.20		133	0	1	134	133	99.3	0.0	0.7	100.0	0.0
64	123.55		54	0	1	55	54	98.2	0.0	1.8	100.0	0.0
65	124.20		113	0	5	118	113	95.8	0.0	4.2	100.0	0.0
66	124.60	a	70	0	2	72	70	97.2	0.0	2.8	100.0	0.0
67	124.60	b	61	0	6	67	61	91.0	0.0	9.0	100.0	0.0
68	125.05		99	0	1	100	99	99.0	0.0	1.0	100.0	0.0
69	125.40		72	0	1	73	72	98.6	0.0	1.4	100.0	0.0
70	126.05		72	0	2	74	72	97.3	0.0	2.7	100.0	0.0
71	126.50	a	86	0	1	87	86	98.9	0.0	1.1	100.0	0.0
72	126.50	b	95	0	2	97	95	97.9	0.0	2.1	100.0	0.0
74	127.00		121	0	1	122	121	99.2	0.0	0.8	100.0	0.0
75	127.30		75	0	0	75	75	100.0	0.0	0.0	100.0	0.0
76	127.85		87	0	1	88	87	98.9	0.0	1.1	100.0	0.0
77	128.15		58	0	7	65	58	89.2	0.0	10.8	100.0	0.0
78	128.65	a	51	0	3	54	51	94.4	0.0	5.6	100.0	0.0
79	128.65	b	105	0	3	108	105	97.2	0.0	2.8	100.0	0.0
80	128.95		92	0	0	92	92	100.0	0.0	0.0	100.0	0.0
81	129.40		102	0	0	102	102	100.0	0.0	0.0	100.0	0.0
82	130.10		57	0	39	96	57	59.4	0.0	40.6	100.0	0.0
83	130.30	a	12	0	4	16	12	75.0	0.0	25.0	100.0	0.0
84	130.30	b	134	0	0	134	134	100.0	0.0	0.0	100.0	0.0
85	130.85		52	0	0	52	52	100.0	0.0	0.0	100.0	0.0
86	131.00		44	0	8	52	44	84.6	0.0	15.4	100.0	0.0
87	131.40	a	31	0	0	31	31	100.0	0.0	0.0	100.0	0.0
88	131.40	b	36	0	0	36	36	100.0	0.0	0.0	100.0	0.0
89	132.20		38	0	13	51	38	74.5	0.0	25.5	100.0	0.0
90	132.65	b	122	1	2	125	123	97.6	0.8	1.6	99.2	0.8
91	132.65	a	7	0	0	7	7	100.0	0.0	0.0	100.0	0.0
92	132.90		38	0	8	46	38	82.6	0.0	17.4	100.0	0.0

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	8-16 mm Chert/ other (#)	8-16 mm Dolomite chips (#)	8-16 mm Coal/ Slag (#)	8-16 mm Total with coal (#)	8-16 mm Total w/o coal (#)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)	8-16 mm Coal/ Slag (%)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)
93	133.30		20	0	1	21	20	95.2	0.0	4.8	100.0	0.0
94	133.70		6	0	0	6	6	100.0	0.0	0.0	100.0	0.0
95	134.00		32	8	5	45	40	71.1	17.8	11.1	80.0	20.0
96	134.50		41	3	1	45	44	91.1	6.7	2.2	93.2	6.8
97	135.00		24	0	0	24	24	100.0	0.0	0.0	100.0	0.0
98	135.50		47	5	2	54	52	87.0	9.3	3.7	90.4	9.6
99	136.00		45	3	1	49	48	91.8	6.1	2.0	93.8	6.3
100	136.30		79	2	9	90	81	87.8	2.2	10.0	97.5	2.5
101	136.90		53	3	0	56	56	94.6	5.4	0.0	94.6	5.4
102	137.40		53	1	3	57	54	93.0	1.8	5.3	98.1	1.9
103	138.00		35	1	2	38	36	92.1	2.6	5.3	97.2	2.8
104	138.50		9	1	0	10	10	90.0	10.0	0.0	90.0	10.0
105	139.00		52	3	3	58	55	89.7	5.2	5.2	94.5	5.5
106	139.50		35	1	1	37	36	94.6	2.7	2.7	97.2	2.8
107	140.00	a	112	1	24	137	113	81.8	0.7	17.5	99.1	0.9
108	140.00	b	33	4	4	41	37	80.5	9.8	9.8	89.2	10.8
109	140.80		64	6	17	87	70	73.6	6.9	19.5	91.4	8.6
110	141.50		53	2	5	60	55	88.3	3.3	8.3	96.4	3.6
111	141.85		28	0	3	31	28	90.3	0.0	9.7	100.0	0.0
112	142.30		62	4	36	102	66	60.8	3.9	35.3	93.9	6.1
113	142.80		49	3	6	58	52	84.5	5.2	10.3	94.2	5.8
114	143.20		93	13	11	117	106	79.5	11.1	9.4	87.7	12.3
115	143.70		59	3	19	81	62	72.8	3.7	23.5	95.2	4.8
116	144.10		37	4	21	62	41	59.7	6.5	33.9	90.2	9.8
117	144.50		115	6	7	128	121	89.8	4.7	5.5	95.0	5.0
118	145.00	a	25	7	3	35	32	71.4	20.0	8.6	78.1	21.9
119	145.00	b	26	4	1	31	30	83.9	12.9	3.2	86.7	13.3
120	145.40		74	4	6	84	78	88.1	4.8	7.1	94.9	5.1
121	145.90		21	1	1	23	22	91.3	4.3	4.3	95.5	4.5

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	8-16 mm Chert/ other (#)	8-16 mm Dolomite chips (#)	8-16 mm Coal/ Slag (#)	8-16 mm Total with coal (#)	8-16 mm Total w/o coal (#)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)	8-16 mm Coal/ Slag (%)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)
122	146.30		66	12	1	79	78	83.5	15.2	1.3	84.6	15.4
123	146.70		45	4	5	54	49	83.3	7.4	9.3	91.8	8.2
124	147.00	a	4	0	1	5	4	80.0	0.0	20.0	100.0	0.0
125	147.00	b	1	0	2	3	1	33.3	0.0	66.7	100.0	0.0
126	147.40		99	6	31	136	105	72.8	4.4	22.8	94.3	5.7
127	148.05		126	8	1	135	134	93.3	5.9	0.7	94.0	6.0
128	148.50		83	0	15	98	83	84.7	0.0	15.3	100.0	0.0
129	148.90		79	2	1	82	81	96.3	2.4	1.2	97.5	2.5
130	149.80		86	6	0	92	92	93.5	6.5	0.0	93.5	6.5
131	150.20		88	9	1	98	97	89.8	9.2	1.0	90.7	9.3
132	150.70		120	6	6	132	126	90.9	4.5	4.5	95.2	4.8
133	151.70		49	0	2	51	49	96.1	0.0	3.9	100.0	0.0
134	152.40		33	7	2	42	40	78.6	16.7	4.8	82.5	17.5
135	152.80		4	1	0	5	5	80.0	20.0	0.0	80.0	20.0
136	153.30		24	1	1	26	25	92.3	3.8	3.8	96.0	4.0
137	153.40		58	16	0	74	74	78.4	21.6	0.0	78.4	21.6
138	153.70		43	4	0	47	47	91.5	8.5	0.0	91.5	8.5
139	154.70		0	0	0	0	0	0.0	0.0	0.0	0.0	0.0
140	155.10		46	11	0	57	57	80.7	19.3	0.0	80.7	19.3
141	155.60		34	4	17	55	38	61.8	7.3	30.9	89.5	10.5
142	156.00		43	3	5	51	46	84.3	5.9	9.8	93.5	6.5
143	156.80		52	3	0	55	55	94.5	5.5	0.0	94.5	5.5
144	157.60		35	3	2	40	38	87.5	7.5	5.0	92.1	7.9
145	158.00		47	3	1	51	50	92.2	5.9	2.0	94.0	6.0
146	158.10		26	1	12	39	27	66.7	2.6	30.8	96.3	3.7
147	158.50		75	2	1	78	77	96.2	2.6	1.3	97.4	2.6
148	159.50		63	0	6	69	63	91.3	0.0	8.7	100.0	0.0
149	159.90		147	2	6	155	149	94.8	1.3	3.9	98.7	1.3
150	160.35		86	2	4	92	88	93.5	2.2	4.3	97.7	2.3

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	8-16 mm Chert/ other (#)	8-16 mm Dolomite chips (#)	8-16 mm Coal/ Slag (#)	8-16 mm Total with coal (#)	8-16 mm Total w/o coal (#)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)	8-16 mm Coal/ Slag (%)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)
151	160.80		80	0	7	87	80	92.0	0.0	8.0	100.0	0.0
152	161.40		81	3	0	84	84	96.4	3.6	0.0	96.4	3.6
153	162.10		65	1	6	72	66	90.3	1.4	8.3	98.5	1.5
154	162.50	a	76	2	3	81	78	93.8	2.5	3.7	97.4	2.6
155	162.50	b	55	0	3	58	55	94.8	0.0	5.2	100.0	0.0
156	163.00		90	2	6	98	92	91.8	2.0	6.1	97.8	2.2
157	163.35		44	2	2	48	46	91.7	4.2	4.2	95.7	4.3
158	163.70		102	4	8	114	106	89.5	3.5	7.0	96.2	3.8
159	164.10		52	6	2	60	58	86.7	10.0	3.3	89.7	10.3
160	164.50		53	1	6	60	54	88.3	1.7	10.0	98.1	1.9
161	165.00		43	3	3	49	46	87.8	6.1	6.1	93.5	6.5
162	165.20		114	3	3	120	117	95.0	2.5	2.5	97.4	2.6
163	165.50		66	0	4	70	66	94.3	0.0	5.7	100.0	0.0
164	165.90	a	34	0	3	37	34	91.9	0.0	8.1	100.0	0.0
165	165.90	b	93	1	1	95	94	97.9	1.1	1.1	98.9	1.1
166	166.25		68	3	0	71	71	95.8	4.2	0.0	95.8	4.2
167	166.40		61	1	8	70	62	87.1	1.4	11.4	98.4	1.6
168	166.90		87	6	1	94	93	92.6	6.4	1.1	93.5	6.5
169	167.00	a	56	1	1	58	57	96.6	1.7	1.7	98.2	1.8
170	167.00	b	58	2	0	60	60	96.7	3.3	0.0	96.7	3.3
171	167.20		75	2	0	77	77	97.4	2.6	0.0	97.4	2.6
172	167.50		98	5	3	106	103	92.5	4.7	2.8	95.1	4.9
173	168.10	a	104	3	2	109	107	95.4	2.8	1.8	97.2	2.8
174	168.10	b	45	2	2	49	47	91.8	4.1	4.1	95.7	4.3
175	168.80		82	3	2	87	85	94.3	3.4	2.3	96.5	3.5
176	168.85		87	3	5	95	90	91.6	3.2	5.3	96.7	3.3
177	169.15		81	1	0	82	82	98.8	1.2	0.0	98.8	1.2
178	169.20		89	1	2	92	90	96.7	1.1	2.2	98.9	1.1
179	169.80		38	2	0	40	40	95.0	5.0	0.0	95.0	5.0

			Counts					Total Percentages with Coal			Total Percentages NO coal	
Lab #	R-Km/ location	Dup	8-16 mm Chert/ other (#)	8-16 mm Dolomite chips (#)	8-16 mm Coal/ Slag (#)	8-16 mm Total with coal (#)	8-16 mm Total w/o coal (#)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)	8-16 mm Coal/ Slag (%)	8-16 mm Chert/ other (%)	8-16 mm Dolomite chips (%)
180	170.00		75	1	1	77	76	97.4	1.3	1.3	98.7	1.3
181	170.05		58	1	1	60	59	96.7	1.7	1.7	98.3	1.7