Missouri Department of Natural Resources
Water Protection Program

Total Maximum Daily Loads (TMDL)

for

Mississippi River
Jefferson County, Missouri

Completed: December 6, 2010
Approved: December 9, 2010

Total Maximum Daily Loads (TMDLs) for Mississippi River
Pollutants: Lead and Zinc

Name: Mississippi River

Location: Jefferson County, Missouri

Nearby Cities: Herculaneum

Hydrologic Unit Code (HUC): 07140101-150005

Water Body Identification Number and Missouri Stream Classification[1]:
1707 – Mississippi River Class P

Designated Beneficial Uses[2] of Mississippi River:
- Livestock and Wildlife Watering
- Protection of Warm Water Aquatic Life
- Protection of Human Health (Fish Consumption)
- Irrigation
- Whole Body Contact Recreation – Category B[3]
- Secondary Contact Recreation
- Drinking Water Supply
- Industrial

Length and Legal Description of Impaired Segment:
Size of Impaired Segment: 195.5 miles
Size of Impairment within segment: 5 miles
Location of Impaired Segment: Dam #27 to confluence with Ohio River
Location of Impairment within segment: From Herculaneum to Selma

Uses that are impaired: Protection of Warm Water Aquatic Life
Protection of Human Health (Fish Consumption)

Pollutants: Lead and Zinc

Pollutant Source: Herculaneum Smelter

TMDL Priority Ranking: High

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[1] For stream classifications see 10 CSR 20-7.031(1)(F). Class P streams maintain permanent flow even during drought conditions.

[2] For beneficial uses see 10 CSR 20-7.031(1)(C) and Table (H)

[3] This category applies to waters designated for whole body contact recreation not contained within Category A. See 10 CSR 20-7.031(1)(C)8.B.

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1. Introduction

This Mississippi River Total Maximum Daily Load, or TMDL, is being established in accordance with Section 303(d) of the Clean Water Act. This water quality limited segment near Herculaneum, Mo. in Jefferson County is included on the U.S. Environmental Protection Agency-approved Missouri 2008 303(d) List of impaired waters with the pollutants of concern being lead and zinc.

The purpose of a TMDL is to determine the pollutant loading a water body can assimilate without exceeding the water quality standards for that pollutant. The TMDL also establishes the pollutant load allocation necessary to meet the Missouri water quality standards established for each water body based on the relationship between pollutant sources and instream water quality conditions. The TMDL consists of a wasteload allocation, a load allocation, and a margin of safety. The wasteload allocation is the portion of the allowable pollutant load that is allocated to point sources. The load allocation is the portion of the allowable pollutant load that is allocated to nonpoint sources. The margin of safety accounts for the uncertainty associated with the model assumptions and data inadequacies. The model used to derive these TMDLs was completed by EPA based on work completed by the EPA contractor Parsons Corporation.

2. Background and Water Quality Problems

The Mississippi River is 2,320 miles long, starting at Lake Itasca in Minnesota and ending at the Gulf of Mexico. The area of interest includes a 5-mile reach of the Mississippi River (Water Body ID: 1707) near Herculaneum, Missouri, located at river mile 151.8 on the Upper Mississippi. This section of the Mississippi River is located in the Cahokia-Joachim Watershed, which is part of the Upper Mississippi River sub-basin within the Mississippi River Basin. The Cahokia-Joachim Watershed's 8-digit Hydrologic Unit Code (HUC) is 07140101.

2.1 Watershed Description

The Herculaneum lead smelter, which has been active since 1892, is located near Joachim Creek at Herculaneum, Mo. in Jefferson County. Approximately 70 percent of the United States' primary lead supply comes from eight mines in southern Missouri, and the Herculaneum smelter constitutes the principal source of refined lead. This smelter has been found to contribute heavy metals to the local environment through wastewater discharges, erosion of slag piles, concentrate transportation and handling, air emission fallout and fugitive emissions. Figure 1 is a map depicting the general location and area around the impaired reach of the Mississippi River near Herculaneum and the smelter. As shown in the map, the impaired reach is downstream of the smelter and the confluence with Joachim Creek. Figure 1 also shows the locations of the wastewater treatment plant outfalls and the water quality/sediment monitoring stations used to support delineation of the impaired segment. All sediment samples used to support this impairment were collected from the Mississippi River. Sediments from Joachim Creek are coarse-grained in nature and lack small-grained sediments that could be sampled.

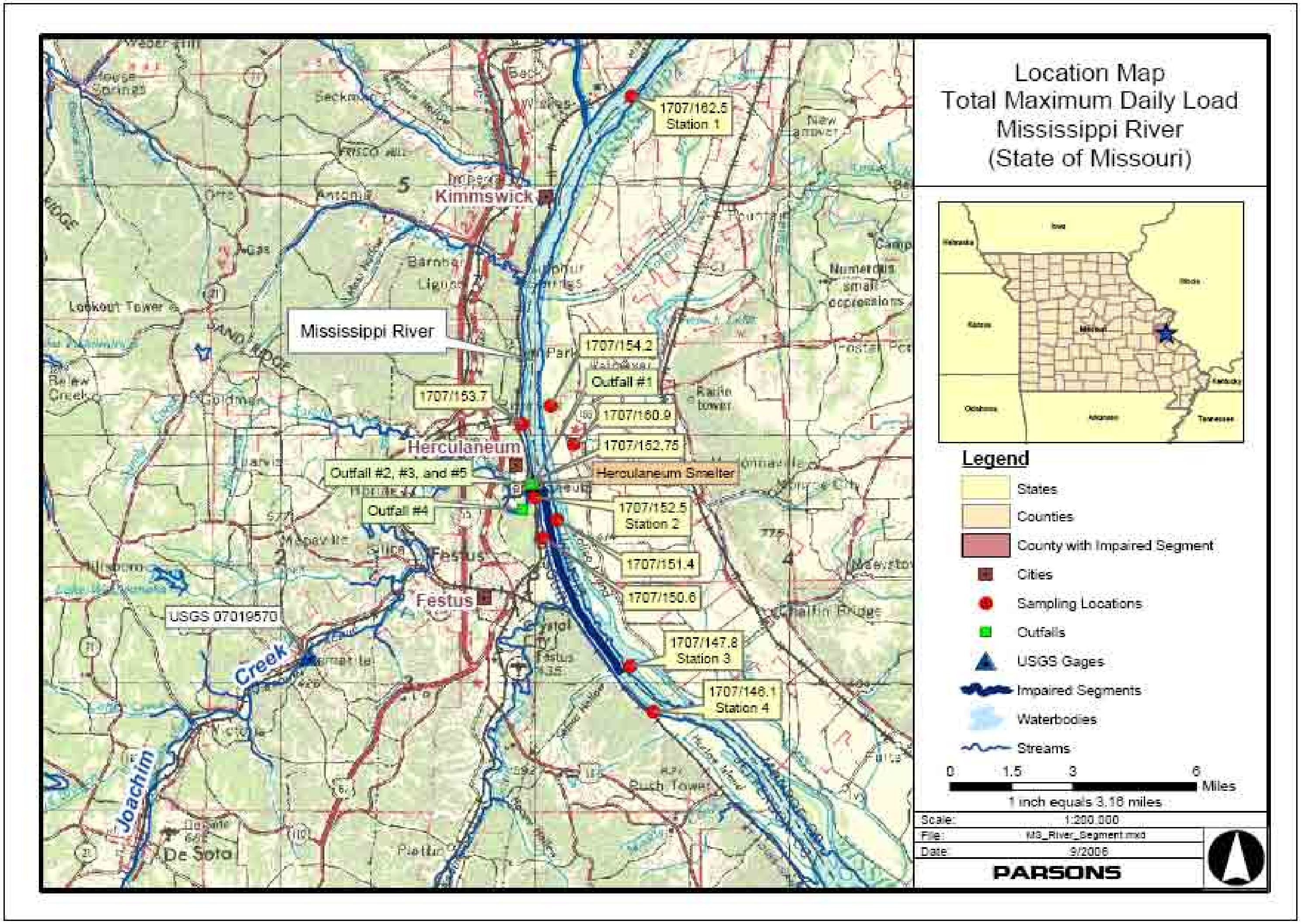

Figure 1. Location of Impaired Reach of the Mississippi River

Due to the limited water quality data available for the Mississippi River, and to best represent the water quality impairment caused by lead and zinc, this TMDL report also includes the subwatershed of Joachim Creek. Figure 2 depicts the general location and area around Joachim Creek, showing the monitoring stations used from this tributary and the specific location of the Herculaneum smelter in relation to the creek.

Figure 3 depicts the general land use categories occurring within the Mississippi River watershed located in the state of Missouri and the Joachim Creek subwatershed. Although the region is known for its extensive historical mines, especially for lead, no mines are known to be active in this region of southeastern Missouri. Because the watershed is rural in nature, land development impacts to water quality from urban activities are expected to be minor.

Tables 1 and 2 show the general land use categories currently recorded within both the Mississippi River watershed and the Joachim Creek subwatershed. Table 1 shows that the Mississippi River subwatershed is dominated by deciduous and evergreen forests (> 60 percent), with significant grasslands (27.5 percent), but very limited agricultural activities (about 2 percent). Urban development only accounts for about 4.7 percent of the land use area within the watershed. Table 2 shows that the Joachim Creek subwatershed is dominated by deciduous and evergreen forests (greater than 50 percent) and grasslands (22.9 percent), with very little agriculture (less than 5 percent). Urban development constitutes 11.7 percent of the total land use within the subwatershed (MoRAP 2005).

Table 1. Land Use Categories for Mississippi River Segment Watershed

Land Use Type	Total Acres	Sq. Miles	% of Total
Barren or Sparsely Vegetated	13,254.70	20.7	0.50%
Cropland	49,850.50	77.9	1.90%
Deciduous Forest	1,455,667.20	2,274.50	55.10%
Deciduous Woody/Herbaceous	136,718.00	213.6	5.20%
Evergreen Forest	70,769.60	110.6	2.70%
Evergreen Woody/Herbaceous	375.1	0.59	0.01%
Grassland	727,379.10	1,136.50	27.50%
Herbaceous-Dominated Wetland	2,602.70	4.07	0.10%
High Density Urban	2,720.80	4.25	0.10%
Impervious	39,843.80	62.25	1.50%
Low Intensity Urban	82,534.30	129	3.10%
Open Water	40,138.00	62.7	1.50%
Woody-Dominated Wetland	20,836.50	32.6	0.79%
TOTAL	**2,642,690.40**	**4,128.60**	**100%**

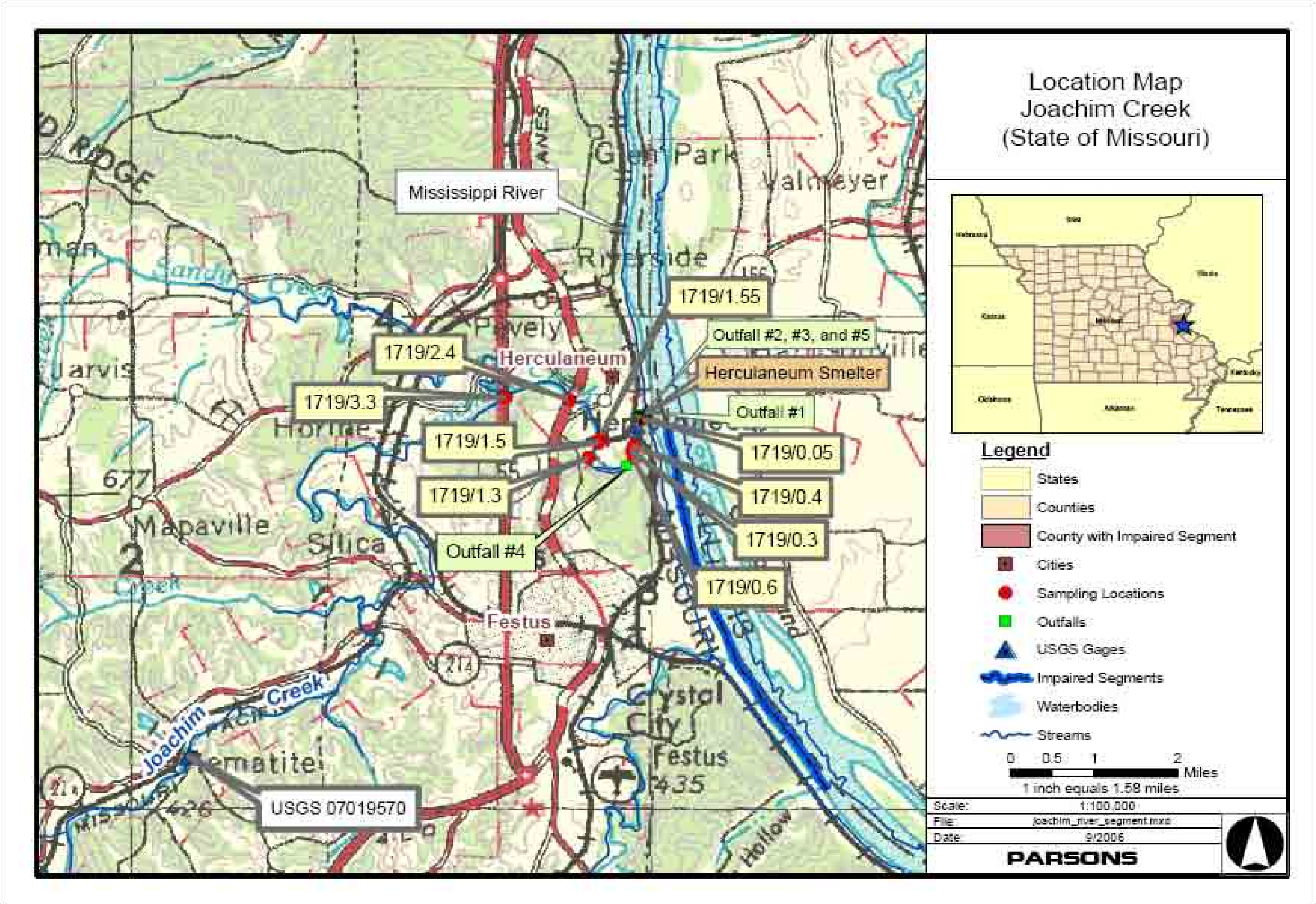

Figure 2. Layout and General Location of Joachim Creek

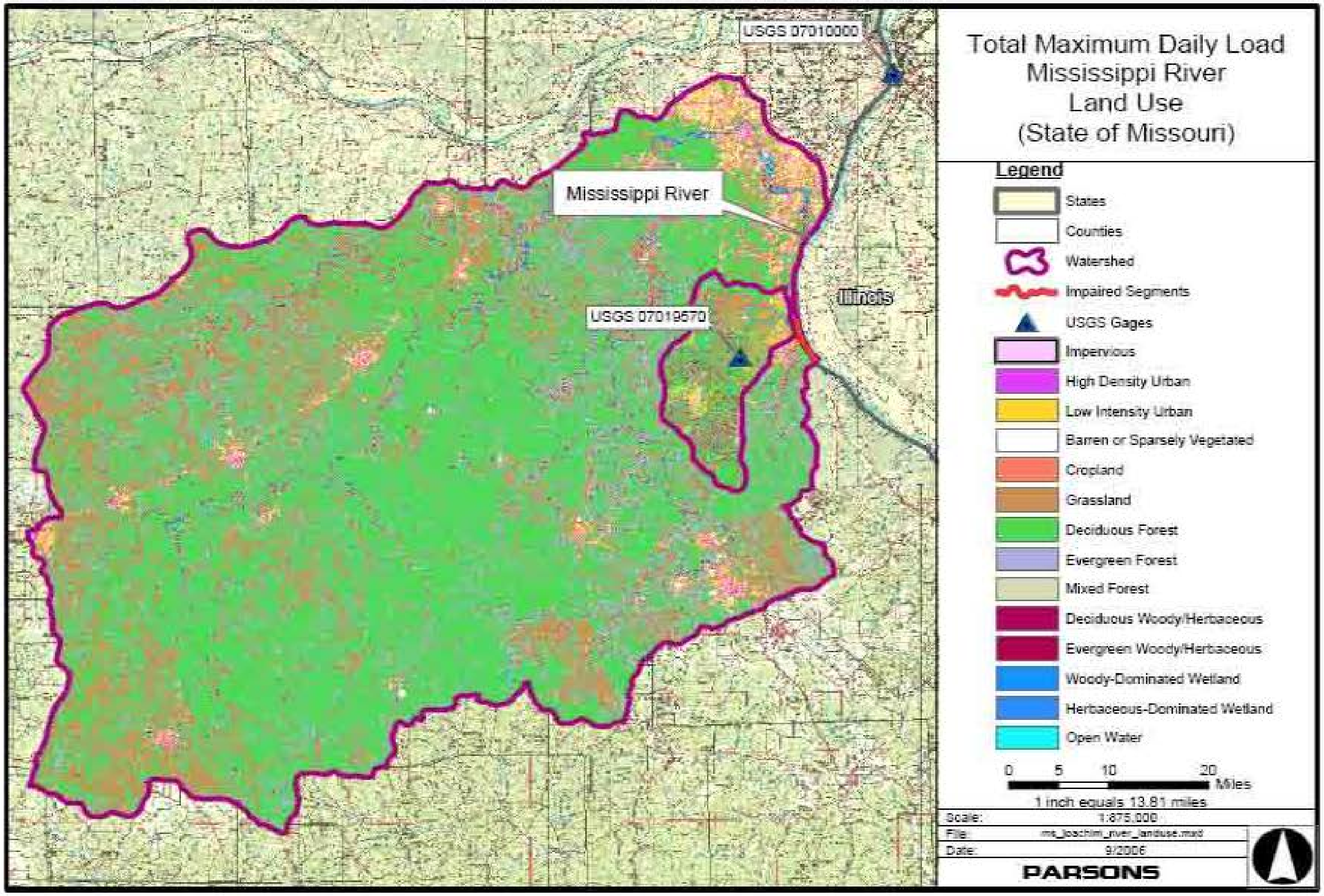

Figure 3. General Land Use Categories

Table 2. Land Use Categories for Joachim Creek

Land Use Type	Acres	Sq. Miles	% of Total
Barren or Sparsely Vegetated	511.4	0.8	0.46%
Cropland	5,115.50	8	4.60%
Deciduous Forest	49,808.90	77.8	44.80%
Deciduous Woody/Herbaceous	5,944.40	9.3	5.40%
Evergreen Forest	6,879.30	10.8	6.20%
Evergreen Woody/Herbaceous	455.2	0.7	0.40%
Grassland	25,475.60	39.8	22.90%
Herbaceous-Dominated Wetland	45.6	0.07	0.04%
High Density Urban	11.9	0.02	0.01%
Impervious	3,535.50	5.5	3.20%
Low Intensity Urban	9,470.50	14.8	8.50%
Open Water	2,390.80	3.7	2.20%
Woody-Dominated Wetland	1,473.20	2.3	1.30%
TOTAL	**111,117.90**	**173.6**	**100%**

2.2 Problem Identification and Current Conditions

Section 303(d) of the Clean Water Act and the EPA Water Quality Planning and Management Regulation (40 CFR Part 130) require states to develop TMDLs for water bodies not meeting applicable water quality standards or designated uses under technology-based controls. TMDLs identify the maximum amount of a pollutant that a water body can assimilate and still meet water quality standards. To determine the maximum pollutant load for a given water body, all existing and readily available data and information must be analyzed to establish both current conditions and future pollutant load reductions.

The only water quality data available for this stretch of the Mississippi River was collected at Station 1707/162.5, upstream of the impaired reach (see Figure 1). Sediment data have been collected from Joachim Creek and from the Mississippi River within the segment of interest. Many attempts to analyze sediment directly from Joachim Creek have failed due to a lack of fine sediments downstream of the smelter. Thus, the majority of the available data consists of Mississippi River sediments sampled downstream of the confluence with Joachim Creek.

In addition to water quality and sediment data, discharge monitoring report[4] data are available for the Doe Run Herculaneum Smelter facility (MO-0000281). The Doe Run Herculaneum Smelter has five permitted outfalls and discharge monitoring report data are available for outfalls 001 and 003 (outfall 002 is combined with 001 as per the permit). Outfalls 004 and 005 are covered under the federal Superfund program (i.e., CERCLA[5]) and are addressed in the operating permit and Administrative Order on Consent, United States Environmental Protection Agency IN MATTER OF: The Doe Run Resources Corporation, Herculaneum, Missouri, Docket Number RCRA-7-2000-

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[4] The form used (including any subsequent additions, revisions, or modifications) to report self-monitoring results by Missouri State Operating Permitting system permittees.

[5] CERCLA – Comprehensive Environmental Response, Compensation and Liability Act

0018/CERCLA-7-2000-0029. For additional information and discussion on the Doe Run Herculaneum Smelter facility, see Source Assessment, Section 3.

Table 3 presents sediment sampling locations and data for Joachim Creek and the Mississippi River. Sampling locations for each water body are listed in upstream to downstream order, and exceedances of sediment and water quality TMDL targets are noted in bold text. Levels of lead and zinc reported in some of the sediment samples for these water bodies are in excess of values commonly reported as toxic to aquatic life, e.g. consensus based threshold and probable effect concentrations as reported by MacDonald et al. (2000). The highest lead value measured in sediment was 26,400 mg/kg at the smelter storm water outfall in Joachim Creek sampled October 2001. The highest zinc concentration was 5,440 mg/kg and collected at the same location and on the same date.

In addition to the data presented in Table 3, preliminary data for lead and zinc in sediment were also collected by the U.S. Fish and Wildlife Service in 1995. Reported values for lead in sediment were 37 mg/kg, 7,720 mg/kg, 7,590 mg/kg, and 23 mg/kg. Three of these values are above the threshold effect concentration value for lead in freshwater sediment of 35.8 mg/kg, and two of the values are above the probable effect concentration of 128 mg/kg (MacDonald et al. 2000). The four reported values for zinc were 101 mg/kg, 29,400 mg/kg, 28,800 mg/kg, and 84 mg/kg. Two of these values are above the threshold effect concentration value for zinc in freshwater sediment of 121 mg/kg, and the same two values are also above the probable effect concentration of 459 mg/kg (MacDonald et al. 2000).

Table 3. Estimated Lead and Zinc Pore water Concentrations Based on Measured Sediment Concentrations

			Sediment Concentration (mg/kg)		Estimated Pore water Concentration (µg/L)	
SITE ID	**SITE NAME**	**Sample Date**	**Pb**	**Zn**	**Pb**	**Zn**
Joachim Creek						
1719/3.3	Joachim Cr. @I-55	1/11/2000	**69.4**	**170**	**17.2**	**320.8**
1719/3.3	Joachim Cr. @I-55	12/6/2001	**57.6**	**161**	**14.2**	**303.8**
1719/2.4	Joachim Cr.@Hwy61 & storm water outfall	12/6/2001	**144**	116	**35.6**	**218.9**
1719/1.5	Joachim Cr. just ab. Dam	12/6/2001	**160**	16.9	**39.6**	31.9
1719/1.55	Joachim Cr. nr. Herc. Smelter	1/11/2000	**162**	**247**	**40.0**	**466.0**
1719/1.55	Joachim Cr. nr. Herc. Smelter (field dup)	1/11/2000	**110**	**167**	**27.2**	**315.1**
1719/1.3	Joachim Cr. 0.2 mi.bl. Dam	12/6/2001	28.7	46.3	**7.1**	87.4
1719/0.6	Joachim Cr. bl. Drainage E. of smelter slag pile	12/6/2001	**61.7**	**192**	**15.3**	**362.3**
1719/0.4	Joachim Cr. 0.2 mi.bl. Drainage E. of slag pile	12/6/2001	**89.8**	116	**22.2**	**218.9**
1719/0.3	Herculaneum Smelter, storm water outfall	10/11/2001	**26,400**	**5,440**	**6,525.9**	**10,264.2**
1719/0.05	Joachim Cr.@ mouth	12/6/2001	**136**	116	**33.6**	**218.9**
Mississippi River above Joachim Creek						
1707/162.5	Mississippi R. 1 mi.ab. Meramec R.	9/27/2001	NA	60	NA	113.2
1707/154.2	Mississippi R. 1.5 mi.ab. Joachim Cr. LDB	12/5/2001	16.9	60.55	4.2	114.2
1707/154.2	Mississippi R. 1.5 mi.ab. Joachim Cr. LDB	7/29/2004	8.06	45.2	2.0	85.3
1707/153.7	Mississippi R. 1 mi.ab. Joachim Cr. RDB	7/29/2004	13.1	56.5	3.2	106.6
1707/160.9	Mississippi R. 1 mi.bl. Meramec R.	12/5/2001	13.7	32.6	3.4	61.5
1707/152.75	Mississippi R.@ smelter outfall, RDB	12/6/2001	**1,710**	**4,920**	**422.7**	**9,283.0**
Mississippi River below Joachim Creek						
1707/152.5	Mississippi R. 0.2 mi.bl. Joachim Cr., RDB	12/5/2001	21.3	33.6	**5.3**	63.4
1707/151.4	Mississippi R. 0.5 mi.bl. Joachim Cr. LDB	7/29/2004	9.02	43.9	2.2	82.8
1707/150.6	Mississippi R. 1.3 mi.bl. Joachim Cr. RDB	7/29/2004	13.25	47.6	3.3	89.8
1707/147.8	Mississippi R. 4.9 mi.bl. Joachim Cr.	12/5/2001	11.7	49.8	2.9	94.0
1707/146.1	Mississippi R. 6.6 mi.bl. Joachim Cr.	12/5/2001	11.8	39.4	2.9	74.3
1707/111	Mississippi R. ab. Chester, Ill.	9/28/2001	NA	75	NA	141.5
1707/43.7	Mississippi R. @ Thebes IL	9/26/2001	NA	61	NA	115.1

Notes: LDB = left descending bank; RDB = right descending bank

Bold indicates exceeded the Threshold Effect Concentration (MacDonald *et al.* 2000) for metals (Pb = 35.8 mg/kg and Zn = 121 mg/kg) or exceeded the chronic TMDL target concentration (Pb = 5.1 µg/L and Zn = 186.8 µg/L)

NA indicates data not available

2.3 Equilibrium Partitioning Approach

Table 3 also shows estimated pore water[6] concentrations for lead and zinc based on measured sediment concentrations. These estimated values are important because, in the absence of measured water quality data, they provide a basis for quantifying TMDL allocations and reductions. The rest of this section provides a detailed discussion of how these values were calculated. Section 3 discusses the methodology for how the estimated values were applied to develop the TMDL. Section 6 provides the TMDL calculations, allocations and reductions necessary to ensure attainment of applicable water quality standards.

The Missouri Department of Natural Resources has not developed numerical guidance or criteria for metals in freshwater sediment. Thus, in order to understand the extent to which lead and zinc in Joachim Creek and Mississippi River sediment could be causing or contributing adverse effects to the aquatic environment, equilibrium partitioning methodology was applied (e.g., USEPA 1996; USEPA 1999; Hassan et al. 1996; McIntosh 1991) to assess the level of lead and zinc contamination in sediment. This procedure involves a number of simplifying assumptions described below. Because both lead and zinc follow well-defined partitioning behavior between pore water and sediment, measured lead and zinc values in sediment were used to estimate potential exposures in the water column based on equilibrium partitioning principles. These principles generally state that when metals reside in sediments they exist in equilibrium with pore water, and when physical-chemical properties are known, the partitioning behavior of metals between the solid (sediment) and aqueous (pore water) phase can be predicted. Pore water concentrations are important because the majority of toxicity from trace metals in the aquatic environment occurs in pore water.

Following the equilibrium partitioning procedure, measured lead and zinc in sediment data were used to back-calculate pore water concentrations. In order to be sufficiently protective of water quality standards, it was assumed that pore water concentrations were in equilibrium with (i.e., the same as) overlying instream concentrations. While this approach may be conservative at higher stream flows where dilution occurs in free-flowing or high-volume water bodies, the approach is appropriately protective of the aquatic environment under critical low flow conditions where dilution is not available. Estimated pore water concentrations may then be compared to hardness-dependent lead and zinc water quality criteria to determine compliance with the water quality standards. Pore water concentrations for heavy metals (Metal_{pw}), such as lead and zinc, are estimated by applying the following equation:

Equation 1: $$\mathbf{Metal_{pw,\,\mu g/L} = Metal_{sed,\,mg/kg}/(K_{d,mL/g})*(1{,}000\ \mu g/mg)}$$

where Metal_{sed} is the heavy metal (i.e., lead or zinc) in sediment concentration and K_d is the distribution coefficient. This equation accurately represents both lead and zinc as both are chemically stable and closely follow equilibrium partitioning principles. Based on K_d (distribution coefficient) values published by EPA (1996, 1999), the appropriate K_d value for lead is 4,045.4 mL/g and the K_d value for zinc is 530 mL/g. In the absence of promulgated numeric criteria or standards for bedded sediments, the threshold effect concentrations for lead and zinc (35.8 mg/kg and 121 mg/kg, respectively) can be used to provide a basis for understanding whether measured sediment concentrations could be contributing to environmental effects (MacDonald et al. 2000).

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[6] Pore water is the water filling the spaces between grains of sediment

Because little or no matched hardness data are available for sediment samples from Joachim Creek and Mississippi River, hardness values for calculating water quality criteria must be estimated. The data used for the water hardness calculation were collected upstream of the impaired reach at Site 1707/162.5 (Mississippi River 1 mile above Meramec River) and resulted in a 25th percentile hardness value of 193 mg $CaCO_3$/L as required by 10 CSR 20-7.031(1)(Y). Based on the assumptions outlined in this section, Table 3 presents estimated lead and zinc equilibrium pore water concentrations for Joachim Creek and Mississippi River. Table 3 also highlights in bold text those estimated pore water concentrations that exceed calculated hardness-dependent chronic water quality criteria for lead and zinc and those sediment concentrations that exceed applicable threshold effect concentrations.

With the exception of one location, the sediment data for the Mississippi River above and below the confluence with Joachim Creek are below the threshold effect concentrations for lead and zinc. The one site with exceedances of the threshold effect concentrations, Site 1707/152.75 (Mississippi River at smelter outfall, right descending bank), exceeded the applicable concentrations for lead and zinc by over a factor of 40 in both cases. The estimated pore water concentrations for this site also exceeded the chronic water quality criteria for lead and zinc. The only other exceedance of chronic water quality criteria for lead and zinc in the Mississippi River was for lead at Site 1707/152.5 two-tenths of a mile below the confluence with Joachim Creek. All site locations on Joachim Creek had exceedances of either applicable lead or zinc threshold effect concentrations, chronic water quality criteria, or both. Because it significantly causes and contributes to lead and zinc toxicity downstream of its confluence with the Mississippi River, Joachim Creek will be included in the TMDL analysis for Mississippi River to account for its contribution to the impairment and to determine whether reductions are necessary to facilitate attainment of downstream water quality standards.

To determine whether the Mississippi River complies with state water quality standards above the impaired reach, Table 4 was developed and compares measured instream water column concentrations from Station 1707/162.5 (Mississippi River, 1 mile above Meramec River) with the chronic water quality criteria for dissolved lead and zinc. Because the sampling location is above the impaired reach and not affected by discharges from the Herculaneum Smelter, these instream values can be regarded as ambient or background concentrations for the Mississippi River.

A comparison of sediment and predicted pore water lead and zinc concentrations at Sites 1707/152.75, 1707/152.5, and 1707/151.4 reflects increasing water quality (i.e., decreasing concentrations) downstream of the Herculaneum Smelter. While ambient water quality data are not available for this area, any difference between potential instream measured concentrations and estimated pore water concentrations is expected to be largely accounted for by dilution from instream flows. However, the use of pore water target concentrations addresses the critical condition and protects benthic[7] invertebrate aquatic life living in close contact with pore water. This target also addresses conditions of low flow, when water column concentrations of lead are likely to be higher as there is less dilution of pore water loading into the water column.

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[7] Existing on the bottom of a water body.

Table 4. Comparison of Paired Acute and Chronic Water Quality Criteria with Instream Lead and Zinc Concentrations for Station 1707/162.5 (Mississippi River 1 mile above Meramec River).

Sample Date	Hardness (mg/L)	Pb acute criterion (µg/L)*	Pb chronic criterion (µg/L)*	Zn acute criterion (µg/L)*	Zn chronic criterion (µg/L)*	Instream Total Concentration (µg/L)		Dissolved Concentration (µg/L)	
						Pb	Zn	Pb	Zn
3/30/2000	193	131.0	5.1	204.6	186.8	2.5	50.0	2.5	50.0
6/27/2001	221	151.3	5.9	229.5	209.6	9.7	50.0	2.5	50.0
9/20/2001	215	146.9	5.7	224.2	204.7	2.5	50.0	2.5	50.0
12/11/2001	245	168.6	6.6	250.4	228.7	2.5	50.0	2.5	50.0
3/21/2002	266	183.9	7.2	268.5	245.2	2.5	50.0	2.5	50.0
6/26/2002	216	147.6	5.8	225.1	205.5	2.5	50.0	2.5	50.0
9/25/2002	189	128.1	5.0	201.0	183.6	2.5	50.0	2.5	50.0
11/26/2002	204	139.0	5.4	214.4	195.8	2.5	50.0	2.5	50.0
3/13/2003	138	91.5	3.6	154.0	140.6	2.5	50.0	2.5	50.0
3/9/04	220	151	6	230	209	8.3	5.0	2.5	5.0
5/25/04	200	136	5	212	193	5.4	5.0	2.5	5.0
9/2/04	170	114	4	185	168	14	5.0	2.5	5.0
3/17/05	230	158	6	238	217	2.5	5.0	2.5	15

* calculated using hardness data collected with the sample

3. Applicable Water Quality Standards and Numeric Water Quality Targets

The ultimate goal of this TMDL is to reduce lead and zinc loading to the Mississippi River and restore water quality. Missouri's water quality standards, found in regulation at 10 CSR 20-7.031, define the state's water quality goals in terms of designated beneficial uses of a water to be maintained and criteria to protect those uses. Discharges to classified streams must comply with both general and specific criteria provided at 10 CSR 20-7.031(3) and (4).

3.1 Designated Beneficial Uses

- Livestock and Wildlife Watering
- Protection of Warm Water Aquatic Life
- Protection of Human Health (Fish Consumption)
- Irrigation
- Whole Body Contact Recreation – Category B
- Secondary Contact Recreation
- Drinking Water Supply
- Industrial

3.2 Uses that are Impaired

- Protection of Warm Water Aquatic Life
- Protection of Human Health (Fish Consumption)

3.3 Antidegradation Policy

Missouri's Water Quality Standards include the EPA three-tiered approach to antidegradation and may be found at 10 CSR 20-7.031(2).

Tier 1 – Protects existing uses and a level of water quality necessary to maintain and protect those uses. Tier I provides the absolute floor of water quality for all waters of the United States. Existing instream water uses are those uses that were attained on or after Nov. 28, 1975, the date of EPA's first Water Quality Standards Regulation.

Tier 2 – Protects and maintains the existing level of water quality where it is better than applicable water quality criteria. Before water quality in Tier 2 waters can be lowered, there must be an antidegradation review consisting of: (1) a finding that it is necessary to accommodate important economic and social development in the area where the waters are located; (2) full satisfaction of all intergovernmental coordination and public participation provisions; and (3) assurance that the highest statutory and regulatory requirements for point sources and best management practices for nonpoint sources are achieved. Furthermore, water quality may not be lowered to less than the level necessary to fully protect the "fishable/swimmable" uses and other existing uses.

Tier 3 – Protects the quality of outstanding national and state resource waters, such as waters of national and state parks, wildlife refuges and waters of exceptional recreational or ecological significance. There may be no new or increased discharges to these waters and no new or increased discharges to tributaries of these waters that would result in lower water quality.

Waters in which a pollutant is at, near or exceeds the water quality criteria are considered in Tier 1 status for that pollutant. Therefore, the antidegradation goal for Mississippi River and Joachim Creek is to restore water quality to a level that meets water quality standards.

3.4 General Criteria

Missouri water quality standards do not contain numeric criteria for metals in sediment. However, elevated levels of lead and zinc in Mississippi River sediment adjacent to and downstream of the Herculaneum smelter represent a violation of the general criteria found in Missouri's water quality standards at 10 CSR 20-7.031(3)(D) and (G). These sections of the general criteria state that:

> *Waters shall be free from substances or conditions in sufficient amounts to result in toxicity to human, animal, or aquatic life.*

And

> *Waters shall be free from physical, chemical, or hydrologic changes that would impair the natural biological community.*

Moreover, 10 CSR 20-7.031(4)(B) of the water quality standards creates a linkage with the general criteria above to the specific criteria for toxic substances by stating:

> *Water contaminants shall not cause the criteria in Tables A and B to be exceeded. Concentrations of these substances in bottom sediments or waters shall not harm benthic organisms and shall not accumulate through the food chain in harmful concentrations, nor shall state and federal maximum fish tissue levels for fish consumption be exceeded.*

Because the Mississippi River is included on Missouri's 2008 303(d) List of impaired waters for lead and zinc in sediment, the ultimate goal of this TMDL is to reduce lead and zinc sediment concentrations such that both general and specific criteria are met for these pollutants.

3.5 Specific Criteria

Both acute and chronic aquatic life protection criteria were evaluated and hardness-dependent criteria values derived for dissolved lead and zinc. Chronic aquatic life protection criteria were chosen as the criteria protective of both acute and chronic toxicity as well as sediment pore water aquatic life exposures that would be chronic in nature rather than subject to short-term fluctuation, as would be characteristic of acute exposures.

Chronic criteria for lead and zinc are derived using equations specified in Missouri's water quality standards at 10 CSR 20-7.031, Table A and expressed as dissolved instream concentrations per 10 CSR 20-7.031(4)(B)2.A.(II). These criteria are hardness dependent and are calculated using the 25th percentile hardness value from available data per 10 CSR 20-7.031(1)(Y) and the following equations:

Equation 2: $$\textbf{Chronic dissolved Pb } (\mu g/L) = e^{(1.273*\ln(\text{Hardness}) - 4.704797)} * (1.46203 - (\ln(\text{Hardness})*0.145712))$$

Equation 3: **Chronic dissolved Zn (µg/L) =** $e^{(0.8473*\ln(\text{Hardness}) + 0.785271)} * 0.986$

In the absence of measured hardness data from the impaired reach of the Mississippi River, the water quality criteria were calculated using the 25th percentile hardness value of 193 mg/L obtained from water quality data collected at Station 1707/162.5 (See Table 3). Dissolved concentrations were calculated using EPA (1996) chronic freshwater criteria conversion factors between total recoverable and dissolved metals when unfiltered samples were analyzed. Conversion factors for lead and zinc are as follows: Pb = 0.695 and Zn = 0.986, the underlying assumption being that most of the unfiltered lead or zinc occurring in a water sample occurs in the dissolved state.

3.6 Flow Estimates

Due to the limited flow data (11 data points) available for the U.S. Geological Survey (USGS) gaging station on Joachim Creek (USGS-07019570), a matched USGS gaging station (USGS-07018100, Big River at Richwoods, MO) was used to calculate flow statistics for Joachim Creek using regression analysis. Because no USGS gaging station was available for the impaired segment of Mississippi River, flow data from USGS-0701000 (Mississippi River at St. Louis, MO), located approximately 17 miles north of Station 1707/162.5, were used to calculate flow statistics for Mississippi River. These data are assumed to be representative of flow near the confluence of Joachim Creek with the Mississippi River. Summary information for USGS gages used for Mississippi River and Joachim Creek flow estimates (i.e., flow duration curves) can be found in Table 5.

Table 5: Summary Information for USGS Gages Used For Flow Duration Curves

Gage Number	Gage Name	Drainage Area (sq. miles)	Time Period Used
USGS-07010000	Mississippi River at St. Louis, Mo.	697,000	01/01/1861 - 09/30/2005
USGS-07019570	Joachim Creek at Hematite, Mo.	95.0	09/22/1961 - 09/14/1967
USGS-07018100	Big River near Richwoods, Mo.	735	04/28/1949 - 09/18/2006

3.7 Numeric Water Quality Targets

Most of the available monitoring data for the lead and zinc impairment of Mississippi River consists of sediment samples collected upstream and downstream of the confluence with Joachim Creek. Analysis of these data indicate lead and zinc contaminated sediment associated with the Herculaneum Smelter are the predominant source of pollutant loading to the impaired segment. Accurately measuring the volume of eroded sediment that have entered Mississippi River would be difficult. Therefore, in the absence of sediment loading data, targeting pore water lead and zinc concentrations becomes a valuable method to address the lead and zinc toxicity impairment associated with the contaminated sediment. The following section provides rationale why pore water lead and zinc resulting from lead and zinc in sediment was adopted to address the lead and zinc impairment:

- Sediment concentrations in Joachim Creek have ranged as high as 26,400 mg/kg for lead and 5,440 mg/kg for zinc. Estimated pore water lead and zinc concentrations for Joachim Creek have consistently exceeded the chronic water quality criteria for these pollutants;

- Sediment concentrations in Mississippi River have ranged as high as 1,710 mg/kg for lead and 4,920 mg/kg for zinc. Estimated pore water lead concentrations exceeded the chronic water quality criterion on one occasion;
- In contrast, downstream sediment samples have predominantly complied with applicable sediment threshold effect concentrations and chronic water quality criteria for lead and zinc;
- It is well recognized that lead is chemically stable and rather strongly sorbs to sediment particles (Hassan et al. (1996); McIntosh (1991));
- Numeric water quality targets set at chronic dissolved lead and zinc concentrations will be protective of the critical condition for benthic and hyporheic[8] fauna as well as higher trophic level aquatic life.

For these reasons, it is reasonable and appropriate to use dissolved lead and zinc in sediment pore water to address impairments for these heavy metals. The use of lead and zinc is a conservative assumption because these metals are known to be more toxic than sediment in an aquatic ecosystem. The lead and zinc TMDL endpoints are hardness-dependent chronic criteria derived using Equation 2 and Equation 3, respectively, from Missouri's Water Quality Standards and expressed as dissolved concentrations. The dissolved lead and zinc TMDL targets are 5.1 μg/L and 186.8 μg/L, respectively. Additional lead and zinc targets for Mississippi River and Joachim Creek are set such that the mass of lead and zinc in a given quantity of sediment are below the consensus based Threshold Effect Concentrations of 35.8 mg/kg and 121 mg/kg for lead and zinc, respectively (MacDonald et al. 2000).

4. Source Inventory and Assessment

Source assessment characterizes known and suspected sources of pollutant loading to the impaired water body. Pollutant sources identified within the watershed are categorized and quantified to the extent information is available. Sources of lead and zinc may be point (regulated) or nonpoint (unregulated) in nature.

4.1 Point Sources

Point sources are defined under Section 502(14) of the Clean Water Act and are typically regulated through the Missouri State Operating Permit program[9] and include any discernible, confined and discrete conveyance, such as a pipe, ditch, channel, tunnel or conduit, by which pollutants are transported to a water body. The only known permitted point source in the watershed for which a Missouri State Operating permit has been issued is the Doe Run Herculaneum Smelter (MO-0000281), owned and operated by the Doe Run Company. It is located in Jefferson County and has five outfalls, four of which discharge into the Mississippi River and one into Joachim Creek. In its renewal application, the company requested authorization to continue to discharge treated process wastewater and process storm water to the Mississippi River through Outfall #001. Outfall #002 historically discharged excess storm water, but was recently capped and has not discharged within the past five years. Outfall 003 discharges acid plant non-contact cooling water without treatment to the Mississippi River. Discharges from Outfalls #001, #002, and #003 are subject to effluent

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[8] Existing in the subsurface of a streambed..

[9] The Missouri State Operating Permitting system is Missouri's program for administering the federal National Pollutant Discharge Elimination System (NPDES) program

limitation given in 40 CFR Part 421 nonferrous metals guidelines, as well as the State of Missouri's effluent regulations and water quality standards provided at 10 CSR 20-7. Discharge Monitoring Report, or DMR, data for Outfalls #001 and #003 can be found in Appendix A.

Discharge monitoring report data available for Outfalls #001 and #003 indicate discharge concentrations to the Mississippi River may have the potential to cause or contribute to the lead and zinc impairment. Because the current operating permit is expired, a reasonable potential analysis per 40 CFR 122.44 (d)(1)(i) must be conducted at renewal to determine whether effluent limit guidelines or water quality based effluent limits are required in the permit. However, technology based limits dictated by 40 CFR 421.72-73 may be lower than the resulting water quality based limits, and are unaffected by Reasonable Potential Analysis. Technology based limits for this type of source must be recalculated at renewal because they vary based on production at the facility. Discharge Monitoring Report data are not available for Outfalls #004 and #005. These outfalls discharge storm water runoff from the slag storage area and facility railroad tracks and staging area, respectively. For these outfalls, the Herculaneum Smelter operating permit indicates that "All Parameters, Effluent Limits, Monitoring and Reporting will be addressed in the Administrative Order on Consent, United States Environmental Protection Agency IN MATTER OF: The Doe Run Resources Corporation, Herculaneum, Missouri, Docket Number RCRA-7-2000-0018/CERCLA-7-2000-0029, as outlined in the statement of work appendix A.IV. and A.V, which is attached to and by reference made a part of this permit." Although the state operating permit is expired, activities covered by the Administrative Order Consent are underway. Additional information can be found in Section 9, Implementation Plans, of this document.

The Herculaneum Smelter has been listed as the cause of the lead and zinc impairment in the Mississippi River. Analysis of the lead and zinc in sediment data found in Table 3 indicate the vast majority of the pollutant loading occurs due to storm water runoff into Joachim Creek adjacent to and from the facility. Metals in sediment data are highest in Joachim Creek in the area around Outfall #004 and reflect extremely high lead (26,400 mg/kg) and zinc (5,440 mg/kg) concentrations. This area drains the main slag storage area, which is a pile covering approximately 30 acres of the smelter plant property located south of the facility. This slag pile is in an area classified as a wetland, and the area experiences periodic flooding. Seepage from the slag pile is therefore another possible source of lead and zinc contamination in addition to storm water runoff. Other areas of Joachim Creek adjacent to the Herculaneum facility also exhibit elevated levels of lead and zinc in sediment, although not as great as the area below the slag storage area. Regardless of provenance, lead and zinc contaminated sediment in Joachim Creek are transported downstream during storm events and are deposited in Mississippi River sediments when Joachim Creek velocities decrease rapidly upon confluence with the larger water body.

Air deposition from the Herculaneum smelter is an historic and current source of lead and zinc contamination to the Joachim Creek and Mississippi River watersheds. Lead and zinc fallout from the smelter contaminates yards and other areas within the watershed that then contribute fine grained contaminated sediment to nearby water bodies. Road dust containing lead and zinc generated along the haul routes in Herculaneum is another source of metals that can contribute to contaminated storm water runoff. Waste rock and spent ore have also historically been used for roads and other construction in the area and, if present, can contribute lead and zinc to the impaired segment. The volume of contamination coming from these sources relative to the pollutant loading from larger sediment sizes such as the slag pile area is not known. Engineered and institutional controls at the slag pile area should reduce the future amount of lead and zinc from this source to Joachim Creek and the Mississippi River. Reduction in emissions and fallout from the Herculaneum smelter should reduce air deposition of lead and zinc from the facility and reduce this source of metals contamination to Joachim Creek and Mississippi River.

4.2 Nonpoint Sources

Nonpoint sources are diffuse sources of pollutant loading that typically cannot be identified as entering a waterbody at a single location. These sources involve runoff from areas not associated with the Herculaneum Smelter that may contribute lead and zinc to surface waters as a result of runoff-producing storm events. Some examples include off-site haul and access roads not constructed of waste rock or spent lead and zinc ore. When compared to the Herculaneum Smelter and historic source areas (i.e., Herculaneum slag pile) of lead and zinc, nonpoint source loading is expected to be minor. While the available literature indicate some amount of lead and zinc in surface materials within Jefferson County (USGS 1984), undisturbed and vegetated areas within the watershed are expected to be insignificant sources of dissolved lead and zinc to the impaired segment.

Other potential sources of lead include storm water runoff from roads, highways, and parking lots that may contain tire residues, exhaust fumes, battery fluid, and motor oil. However, these sources are not expected to be significant contributors to the impairment. Minor contributions from Iowa and Illinois are also expected and are quantified as background loading for this TMDL. Currently, there are no known significant sources of lead and zinc from these areas, and the river segment of interest is not listed as impaired in Illinois.

5. Technical Approach and Methodology

A TMDL is the maximum pollutant load that a water body can assimilate and still attain water quality standards. A TMDL is expressed as the sum of all wasteload allocations (point source loads), load allocations (nonpoint source loads), and an appropriate margin of safety, which accounts for uncertainty concerning the relationship between effluent limitations, modeling and water quality. The TMDL, which is also known as the load capacity of the water body, can be expressed by the following equation:

Equation 4: $$\mathbf{TMDL = LC = \sum WLA + \sum LA + MOS}$$

Where LC is the load capacity, ∑WLA is the sum of all wasteload allocations, ∑LA is the sum of all load allocations, and MOS is the margin of safety. The objective of the TMDL is to estimate allowable pollutant loads and to allocate these loads to known pollutant sources within the watershed so appropriate control measures can be implemented and the water quality standard achieved. The Code of Federal Regulations (40 CFR § 130.2 (1)) states that TMDLs can be expressed in terms of mass per time, toxicity, or other appropriate measures. For lead and zinc contamination, TMDLs are expressed as pounds per day using a load duration curve. The load duration curve represents the maximum one-day load the water body can assimilate and maintain the water quality criterion.

5.1 Developing a Load Duration Curve

Load duration curves were calculated for dissolved lead and zinc by multiplying estimated flow values for the outlets of the Mississippi River impaired reach and Joachim Creek by the chronic criteria for dissolved lead and zinc. Load duration curves were developed for Joachim Creek after sediment data and source inventory analysis revealed contaminated sediment loading from the water body was having a negative impact on water quality in Mississippi River. Units for all load duration curves are pounds of dissolved lead or zinc per day. The TMDLs were plotted as load duration curves and were used to derive wasteload allocations and load allocations for each segment. The lead and zinc sediment targets were set using the percent of lead and zinc in a given mass of sediment such that the Threshold Effect Concentrations are below the target level. Results and calculations are presented in Section 6.

5.2 Deriving Chronic Dissolved Lead and Zinc Criterion to Support the TMDL

The chronic criterion values for dissolved lead and zinc were calculated using Equation 2 and Equation 3, respectively, and the 25th percentile water hardness value per 10 CSR 20-7.031(1)(Y). In light of the above, normality testing may be required to ensure that the appropriate 25th percentile value is used to support the hardness calculations. The water hardness dataset was statistically tested for normality and the results used to determine if log-transformation of the data would be necessary. For the water hardness data, results of normality testing indicated that these data were not normally distributed and it was necessary to log-transform the data before the hardness calculations could be completed. The resulting hardness value of 193 mg/L was then used to derive dissolved lead and zinc chronic criterion of 5.1 μg/L and 186.8 μg/L, respectively.

5.3 Stepwise Explanation of How TMDL Calculations were Performed

The following discussion provides a summary of the steps involved in the calculation of key components of the Mississippi River TMDLs for lead and zinc. The following discussion provides a summary of the steps involved in the calculation of load duration curves. Load duration curves form the basis of the TMDL and are the benchmark from which pollutant load reductions are calculated.

Step 1: Develop a flow duration curve. A flow duration curve is a graph depicting the percent of time in which a given flow is equaled or exceeded. Flow duration curve analysis identifies intervals, which can be used as a general indicator of hydrologic condition (i.e., wet versus dry and to what degree). This indicator can help point problem solution discussions towards relevant watershed processes, important contributing areas, and key delivery mechanisms. These are all important considerations when identifying those controls that might be most appropriate under certain conditions (Cleland 2002).

Flow duration curves for the Mississippi River and Joachim Creek were developed for this TMDL. The associated data set used to plot the flow duration curves is summarized in Appendix B. Continuous discharge data from USGS gaging station USGS-07010000 (Mississippi River at St. Louis, MO) was used to derive the flow duration curve for Mississippi River. Due to limited continuous flow data on Joachim Creek (USGS-07019570, Joachim Creek at Hematite, Mo.), a matched station approach was used by correlating flow conditions with a location having a longer period of record (USGS-07018100, Big River near Richwoods, Mo.). Additional information on the three USGS gaging stations used to derive flow duration curves can be found in Table 5.

In order to estimate flow using a stream gage station with limited data (i.e. Joachim Creek), flows from the station with limited data and a matched station are statistically correlated to yield a useful estimate of flow. Specifically, a regression analysis is conducted to determine whether a statistical relationship exists, and an equation is developed to describe this statistical relationship. A calculated p-value from this equation of less than 0.05 suggests a statistically significant relationship between these variables. In such a case, the station with a statistical correlation would be used as the match station and the stream flow used to support the analysis.

Step 2: Develop load duration curves (TMDLs). Similar to a flow duration curve, the load duration curve depicts the percent of time in which a given dissolved lead or zinc load is equaled or exceeded. When using the chronic dissolved lead or zinc criterion, the resulting curve also represents the TMDL. In brief, the load duration curve is developed by multiplying the stream flows developed in Step 1 by the chronic dissolved lead and zinc criterion and by a unit conversion factor, as summarized by the following equation:

Equation 5. **Load (lb/day) = stream flow (cfs) * criterion (mg/L) * 5.395**

Step 3: Develop load duration curve with Margin of Safety. The margin of safety can be either implicit or explicit. In this case, the margin of safety is implicit due to conservative assumptions involved in the determination and derivation of TMDL target criteria. The margin of safety for this TMDL is further explained in section 6.7 of this document.

Step 4: Estimate current point source loading. The sole point source contributor of lead and zinc to the Mississippi River is the Doe Run Herculaneum Smelter. There are currently four discharges to the Mississippi River from the Herculaneum Smelter, consisting of Outfalls #001, #002, #003 and #005. Outfall #001 is the main discharge outfall and has additional flow from the facility storm water Outfall #002 during wet weather conditions. Outfall #003 discharges non-contact cooling water to the Mississippi River from the acid plant area of the facility. Outfall #005 is covered by the permit, which incorporates certain terms and conditions of the Administrative Order on Consent, as is Outfall #004 that discharges to Joachim Creek. Limited discharge and concentration data are available for these outfalls and should not be considered in determining the current point source loading from the facility. Therefore, current point source loading will be calculated for Outfalls #001 and #003 using the following modified Equation 5:

Equation 6. ***Average current point source loading = maximum detected dissolved Pb/Zn concentration (mg/L) * estimated stream flow from sample date (cfs) * 5.395 (lb/day)***

The estimated current point source loading of lead and zinc can then be used to calculate point source load reductions for the watershed (Step 8).

Step 5: Calculate Wasteload Allocation. The wasteload allocation portion of the TMDL is an instream pollutant allocation expressed as pounds per day (lb/day) and used to allocate pollutant loading to point sources of pollutants within the watershed. Such sources may be diverse and are predominantly subject to permitting requirements. The wasteload allocation is equal to the available load capacity after the margin of safety and load allocation are accounted for.

The predominant land uses (i.e. forest and grassland) within the Mississippi River watershed contribute a negligible amount of dissolved lead and zinc pollutant loading to the water body. While the available literature indicate some amount of lead and zinc in surface materials within Jefferson County (USGS 1984), undisturbed and vegetated areas within the watershed are expected to be insignificant sources of dissolved lead and zinc to the impaired segment. Therefore, it is reasonable to allocate the entire loading capacity for dissolved lead and zinc to point sources as wasteload allocations.

The wasteload allocation for dissolved lead and dissolved zinc at any given percentile flow exceedance can be calculated from the TMDL load duration curve by solving Equation 4 for the wasteload allocation component:

Equation 7. **WLA (lb/day) = TMDL (lb/day) – MOS (lb/day) – LA (lb/day)**

where WLA is the wasteload allocation, MOS is the margin of safety, and LA is the load allocation. Wasteload allocations for dissolved lead and zinc calculated using Equation 7 will be for the combined discharges from the Doe Run Herculaneum Smelter facility and all potential future point sources of lead and zinc to the Mississippi River rather than for individual outfalls.

Step 6: Estimate current nonpoint source loading. For the reasons detailed in Section 4 and in Step 5 above, nonpoint source loading of dissolved lead and zinc to the watershed are expected to be insignificant compared to point source loading of these pollutants. This is generally supported by the lack of impairment for these pollutants in nearby streams and watersheds with similar land use types. Therefore, for the purposes of this TMDL, current nonpoint source loading of dissolved lead and zinc are estimated to be zero.

Step 7: Calculate load allocation. The load allocation is also an instream pollutant allocation expressed in lb/day, similar to the wasteload allocation. It is used to allocate pollutant loading to nonpoint sources of pollutants within a watershed. Such sources may be diverse and difficult to identify and are not subject to permitting requirements. Because the predominant source of dissolved lead and zinc loading to Mississippi River derives from a point source, the load allocation portion of the TMDL is set to zero.

Step 8: Estimate point source load reduction. Point source load reduction was calculated by subtracting the TMDL wasteload allocation (Step 5) from the current point source loading estimate (Step 4) as shown in the following equation:

Equation 8. ***Point source load reduction (lb/day) = Current point source load (lb/day) – TMDL Wasteload Allocation (lb/day)***

The percent point source load reduction can be calculated using the following equation:

Equation 9. ***Percent point source load reduction = (point source load reduction [lb/day]/***

Current point source loading [lb/day]) * 100

As stated in Step 6, load allocation reductions are not necessary because nonpoint source loading of dissolved lead and zinc are expected to be negligible. Results of all the aforementioned calculations are discussed in Section 6.

5.4 Reduction Target

The advantage of the load duration curve approach is avoidance of the constraints associated with using a single-flow critical condition during the development of a TMDL. To determine the amount of load reduction necessary to comply with the chronic criterion for dissolved lead and zinc, instream critical conditions were evaluated. While flow data collected for the Mississippi River and Joachim Creek allowed all flow ranges to be analyzed, percent load reductions for dissolved lead and zinc were predominantly calculated for lower flow conditions.

6. Results of TMDL Calculations and Pollutant Allocations

Following is a discussion of the results of the TMDL calculations and pollutant allocations for the Mississippi River. Calculations were conducted for both Mississippi River and Joachim Creek due to Joachim Creek causing and contributing to the downstream water quality impairment of Mississippi River. Section 5 discussed the specific steps taken to develop each of these components.

6.1 TMDL Calculations

Figure 4 below is a plot comparing flows from USGS 07019570 (Joachim Creek at Hematite, MO) and the matched station USGS 07018100 (Big River at Richwoods, MO) to demonstrate the correlation between flows at these two gauging stations. The regression analysis is necessary because a continuous flow data set is needed to match the available sediment data and there were insufficient flow data (only 11 data points) at the Joachim Creek USGS gage station to plot the flow duration curve.

Figure 4. Correlation of Flow Between USGS 07019570 and Matched Station USGS 07018100

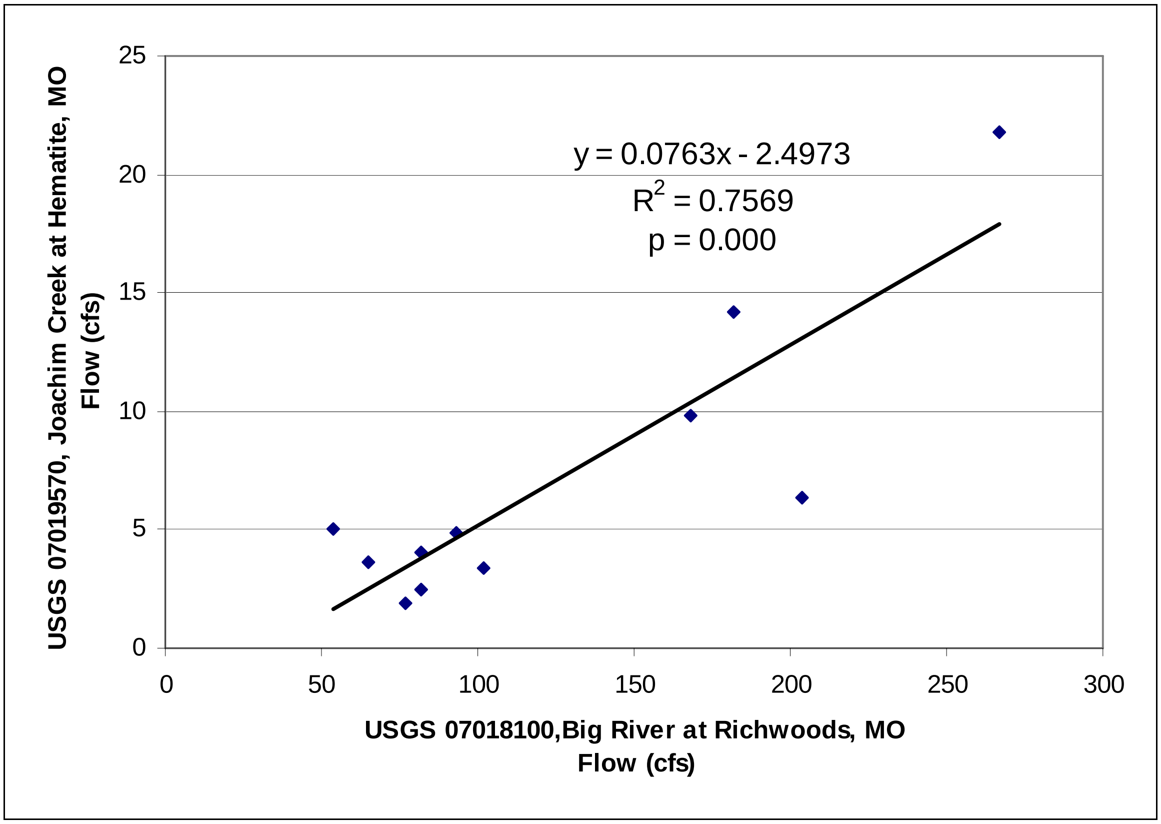


Figure 4 demonstrates the statistical correlation between the two gage stations ($p<0.05$; $r^2 > 0.76$)) and indicates flows at the USGS 07019570 gage station could be estimated using the matched station with a relatively high degree of certainty. Figure 4 also shows the regression equation that was used to support estimates of stream flow.

Figures 5 through 8 present dissolved lead and zinc TMDL load duration curves for Mississippi River and loads in Joachim Creek that should not cause or contribute to the downstream impairment in Mississippi River. Also plotted on Figures 5 through 8 are estimated current loads for dissolved lead and zinc for these water body segments. Estimated current dissolved lead and zinc loads above their respective load duration curve indicate impairment for the pollutant of concern. Complete details on the Mississippi River and Joachim Creek TMDLs can be found in Appendix C.

Figure 5. Chronic Dissolved Lead TMDL for Mississippi River

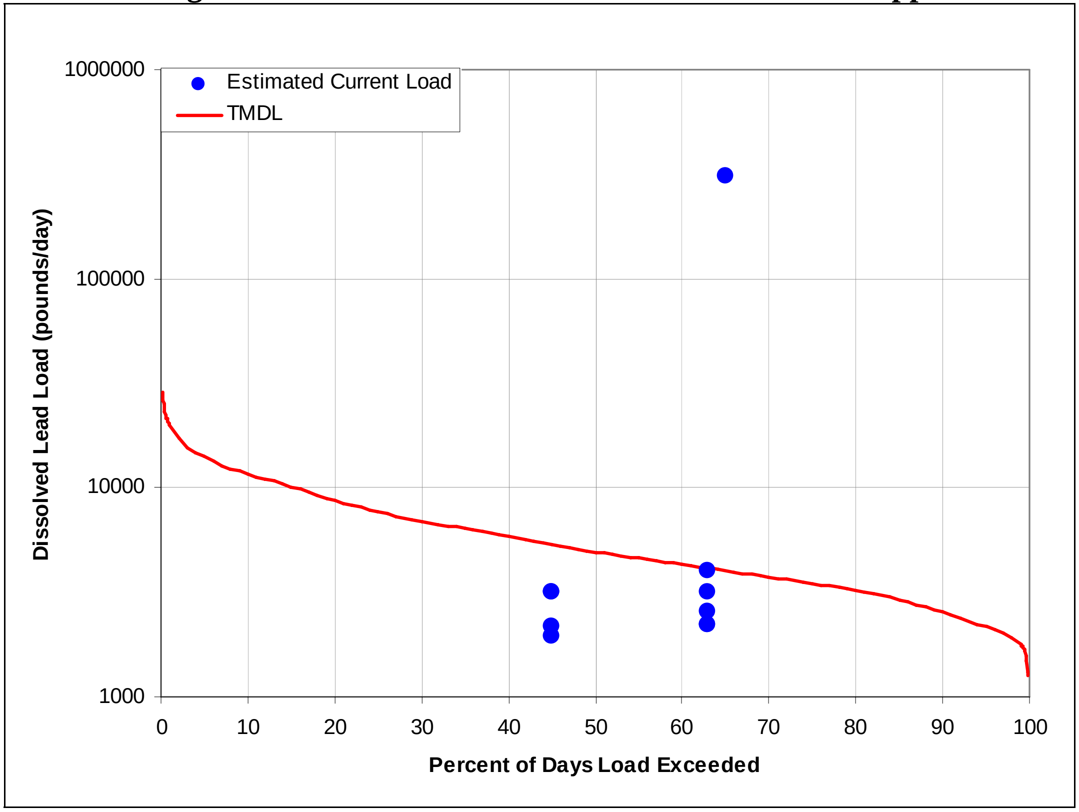


Figure 6. Chronic Dissolved Zinc TMDL for Mississippi River

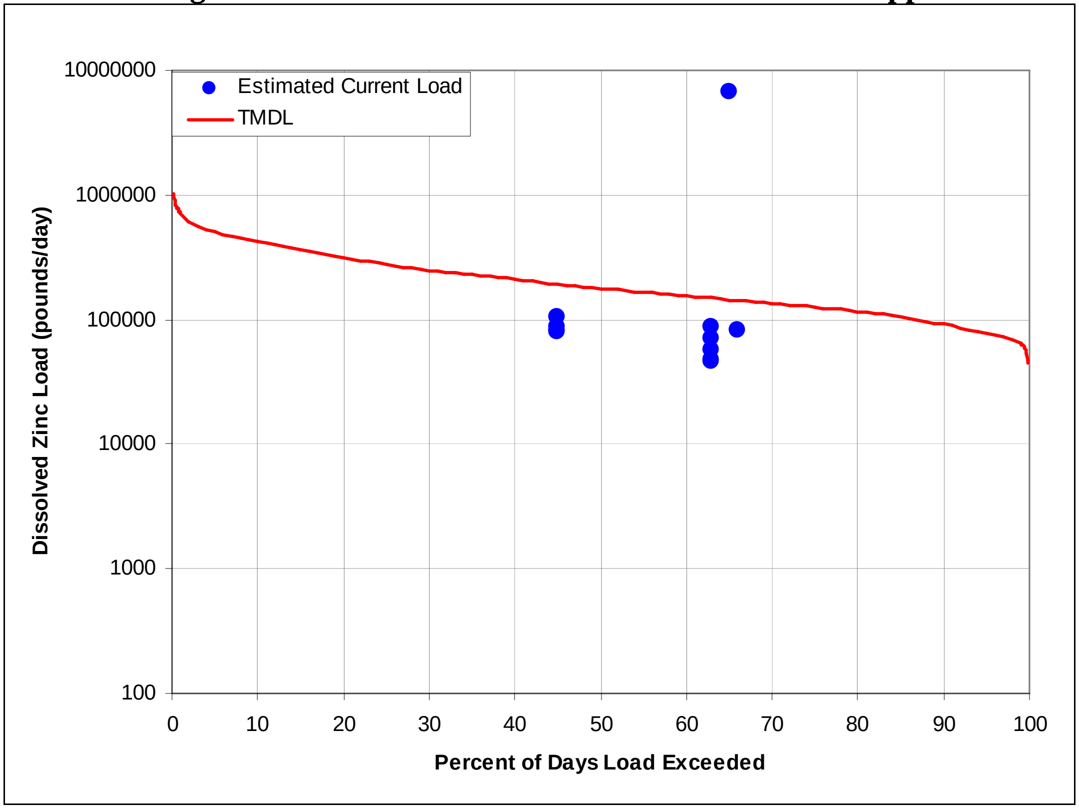


Figure 7. Chronic Dissolved Lead TMDL for Joachim Creek

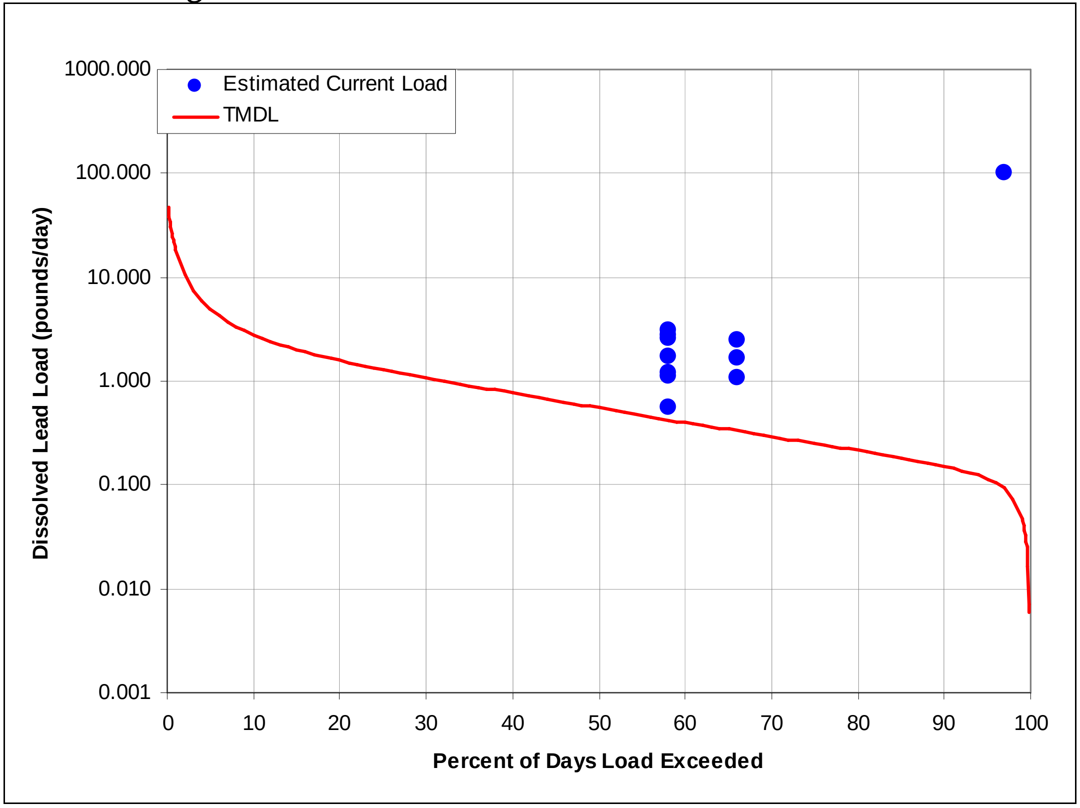
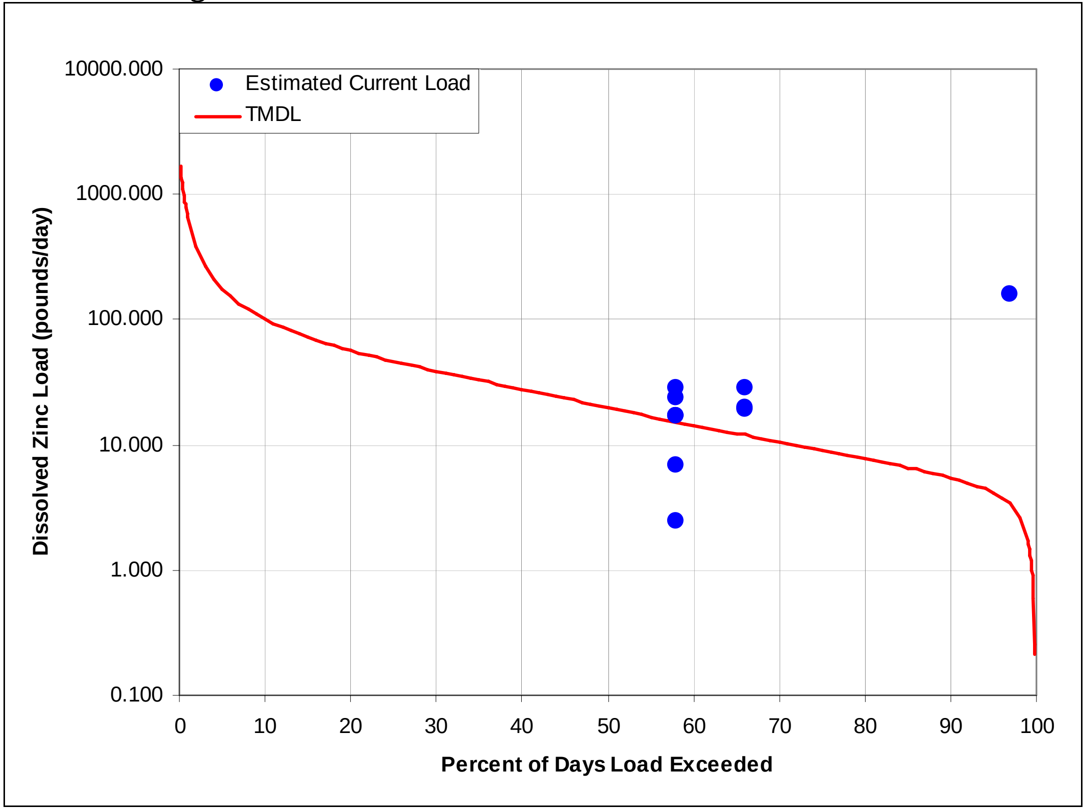


Figure 8. Chronic Dissolved Zinc TMDL for Joachim Creek



6.2 Wasteload Allocations for Mississippi River and Joachim Creek

As discussed in Section 5.3.1, the wasteload allocation for dissolved lead and dissolved zinc at any given percentile flow exceedance can be calculated from the TMDL load duration curve by using the following equation:

WLA (lb/day) = TMDL (lb/day) – MOS (lb/day) – LA (lb/day)

where WLA is the wasteload allocation, MOS is the margin of safety, and LA is the load allocation. Because the MOS for the Mississippi River and Joachim Creek TMDLs are implicit and nonpoint source loading of dissolved lead and zinc to the watershed are expected to be insignificant compared to point source loading of these pollutants, wasteload allocations for dissolved lead and zinc are set equal to the TMDL load capacities for these parameters. Tables 6 and 7 contain Mississippi River TMDL and WLA values for dissolved lead and zinc, respectively. It should be noted that flow values for the Mississippi River in these tables are rounded values. Tables 8 and 9 contain Joachim Creek TMDL and WLA values for dissolved lead and zinc, respectively.

It is very important to note that the allowable WLAs for lead and zinc have been calculated for all potential point sources at various flow conditions, which may include any unpermitted abandoned mines or tailings piles (or future permits) within the Mississippi River and Joachim Creek watersheds. Any WLA, however, does not reflect an authorization to discharge from an unpermitted point source. Discharging lead and zinc to waters of the state without a permit is considered a violation of both state and federal Clean Water Law. Should it become necessary to permit currently unpermitted point sources, those areas must follow the Department of Natural Resources' permit application and antidegradation processes and will be subject to a thorough evaluation in light of this TMDL.

It is also important to note that the Herculaneum Smelter facility will not be receiving the entire calculated WLAs for lead and zinc. This is due to the fact that categorical, technology-based effluent loads at the time of TMDL development are less than the water-quality based loads calculated by the TMDL. The remainder of the WLAs for lead and zinc will be held in reserve for any future point sources, which may include any unpermitted abandoned mines or tailings piles (or future permits), within the Mississippi River and Joachim Creek watersheds.

Table 6. Dissolved Lead Wasteload Allocations for Mississippi River

Percentile flow exceedance	Flow (cfs)	Dissolved Lead TMDL (lbs/d)	Dissolved Lead WLA (lbs/d)	Dissolved Lead LA (lbs/d)	MOS* (lbs/d)
95%	73600	2156	2156	0	-
90%	87000	2549	2549	0	-
70%	128000	3750	3750	0	-
50%	168000	4922	4922	0	-
30%	236000	6915	6915	0	-
10%	395800	11596	11596	0	-
5%	480000	14063	14063	0	-

* The margin of safety, or MOS, is implicit, see Section 7

Table 7. Dissolved Zinc Wasteload Allocations for Mississippi River

Percentile flow exceedance	Flow (cfs)	Dissolved Zinc TMDL (lbs/d)	Dissolved Zinc WLA (lbs/d)	Dissolved Zinc LA (lbs/d)	MOS* (lbs/d)
95%	73600	77800	77800	0	-
90%	87000	91965	91965	0	-
70%	128000	135304	135304	0	-
50%	168000	177587	177587	0	-
30%	236000	249468	249468	0	-
10%	395800	418387	418387	0	-
5%	480000	507392	507392	0	-

* The margin of safety, or MOS, is implicit, see Section 7

Table 8. Dissolved Lead Wasteload Allocations for Joachim Creek

Percentile flow exceedance	Flow (cfs)	Dissolved Lead TMDL (lbs/d)	Dissolved Lead WLA (lbs/d)	Dissolved Lead LA (lbs/d)	MOS* (lbs/d)
95%	3.9	0.115	0.115	0	-
90%	5.1	0.150	0.150	0	-
70%	10.0	0.293	0.293	0	-
50%	18.8	0.551	0.551	0	-
30%	36.5	1.069	1.069	0	-
10%	95.9	2.811	2.811	0	-
5%	167	4.890	4.890	0	-

* The margin of safety, or MOS, is implicit, see Section 7

Table 9. Dissolved Zinc Wasteload Allocations for Joachim Creek

Percentile flow exceedance	Flow (cfs)	Dissolved Zinc TMDL (lbs/d)	Dissolved Zinc WLA (lbs/d)	Dissolved Zinc LA (lbs/d)	MOS* (lbs/d)
95%	3.9	4.14	4.14	0	-
90%	5.1	5.43	5.43	0	-
70%	10.0	10.59	10.59	0	-
50%	18.8	19.86	19.86	0	-
30%	36.5	38.57	38.57	0	-
10%	95.9	101.40	101.40	0	-
5%	167	176.41	176.41	0	-

* The margin of safety, or MOS, is implicit, see Section 7

6.3 Load Allocations for Mississippi River and Joachim Creek

The load allocation, or LA, includes all existing and future nonpoint sources and natural background contributions (40 CFR § 130.2(g)) of the pollutants of concern. Load allocations for the Mississippi River and Joachim Creek TMDLs include all nonpoint sources of dissolved lead and zinc within their respective watersheds. When compared to the Herculaneum Smelter and historic source areas of lead and zinc (i.e., Herculaneum slag pile), nonpoint source loading is expected to be minor. Therefore, the LA components of the Mississippi River and Joachim Creek TMDLs for dissolved lead and zinc are set at zero.

6.4 Point Source Load Reduction

Based on the prior assessment of sources and the distribution of excursions from water quality standards at monitoring locations, the loading of dissolved lead and zinc originates from the Herculaneum Smelter and historic source areas (i.e., Herculaneum slag pile). Miscellaneous land uses and natural background sources contribute a relatively small fraction of the overall pollutant source loading. This is generally supported by water quality data collected from water bodies not likely to be affected by the Herculaneum Smelter and associated areas (i.e. Station 1707/162.5, Mississippi River 1 mile above Meramec River). Therefore, the load reductions necessary to achieve water quality standards will be obtained from the Herculaneum Smelter and historic source areas of lead and zinc.

Effluent concentrations from the Herculaneum Smelter Outfalls #001 and #003, as well as estimated point source loading from these outfalls, can be found in Appendix A. The estimated point source loading for Outfalls #001 and #003 were calculated using methods and equations contained in Section 5.3, Step 4. The 95th percentile concentrations for lead and zinc for each outfall and an estimate of outfall WLA reductions can be found in Table 10. Design flow for Herculaneum Smelter Outfall #001 is 1.224 million gallons per day, or 1.897 cfs. The design flow for Outfall #003 at the facility is 2.33 million gallons per day, or 3.61 cfs.

Due to the absence of contemporaneous effluent and instream data for total recoverable metals, dissolved metals, hardness, and total suspended solids with which to calculate metals translators, partitioning between the dissolved and absorbed phases was assumed to be minimal (Section 5.7.3, EPA/505/2-90-001). Freshwater criteria conversion factors for dissolved metals were used as the metals translator as recommended in guidance (Section 1.3, 1.5.3, and Table 1, EPA 823-B-96-007). All concentrations and loads in Table 10 were calculated in terms of dissolved, rather than total recoverable, lead and zinc concentrations to be comparable with the Mississippi River TMDL.

Table 10. Estimated Herculaneum Smelter Outfall Percent Reductions

Outfall	95th Percentile Effluent Conc. (μg/L)		Current Loading (lb/day)		TMDL Load[1] (lb/day)		Percent Reduction	
	Lead	Zinc	Lead	Zinc	Lead	Zinc	Lead	Zinc
001	131.31	1553.94	1.34	15.9	2156	77800	-99%	-99%
003	139.22	39.44	2.71	0.77			-99%	-99%

1 = Mississippi River TMDL load at the 95th percentile flow exceedance

As shown in Table 10, the current lead and zinc loading from the Doe Run, Herculaneum Smelter facility are below the TMDL wasteload allocations for these pollutants to the Mississippi River. Based upon these calculations, no further reductions should be necessary from facility Outfall #001 to meet the lead and zinc loading requirements of the TMDL to the Mississippi River. Future effluent limitations for the facility operating permit should be based upon the more protective of either technology or water quality-based limitations as per state and federal rule and guidance.

6.5 Nonpoint Source Load Reduction

Because there are minor nonpoint source loading of dissolved lead and zinc to Mississippi River and Joachim Creek, no reduction in nonpoint source loading is necessary under this TMDL. Load reductions will come entirely from point sources as discussed in Section 6.4.

7. Margin of Safety

Federal regulations at 40 CFR 130.7(c)(1) require that TMDLs take into consideration a margin of safety. A margin of safety is required in the TMDL calculation to account for uncertainties in scientific and technical understanding of water quality in natural systems. The margin of safety is intended to account for such uncertainties in a conservative manner. Based on EPA guidance, the margin of safety can be achieved through one of two approaches:

(1) Explicit - Reserve a portion of the load capacity as a separate term in the TMDL.

(2) Implicit - Incorporate the margin of safety as part of the critical conditions for the wasteload allocation and the load allocation calculations by making conservative assumptions in the analysis.

The margin of safety for the Mississippi River TMDL is implicit and based on the conservative assumptions used in developing and applying the TMDL load duration curves. Using the load duration curve approach also ensures water quality standards are achieved under all flow regimes. Additionally, setting dissolved lead and zinc TMDLs for Joachim Creek will ensure loading of dissolved metals to the impaired segment of Mississippi River are reduced. Lastly, setting secondary TMDL targets for Mississippi River and Joachim Creek such that the mass of lead and zinc in a given quantity of sediment are below the consensus based Threshold Effect Concentrations will ensure reductions in source sediment and related toxicity to these water bodies.

This TMDL document was prepared using data and assumptions that contribute a degree of uncertainty to the process. Following is a list of operating assumptions needed to support the TMDL analysis and calculations.

- The most important uncertainty assumption is that the data are measured from bulk stream sediments, and using EqP techniques, stream porewater concentrations were estimated. No instream water quality data were available for the impaired reach of the Mississippi River, and as such, this TMDL is based on measured sediment concentrations.

- Second, although it is known that substantial dilution would occur in both the Mississippi River and Joachim Creek due to large water volumes and high flow velocity, the estimated porewater concentrations based on sediment were used as the mathematical basis of this TMDL for both subwatersheds.

- The DMR data evaluated from the smelter outfalls show no historical excursions above their respective effluent limits, but a large “mixing zone” or dilution capacity is incorporated into these effluent limits, which are well above the state water quality standards for lead and zinc.

- This TMDL focuses on point source discharges from the Herculaneum smelter, including storm water, because this is believed to be the predominant source of lead and zinc residues. No nonpoint sources of lead or zinc within either of the subwatersheds were identified or incorporated into the TMDL report.

- The estimated flow for the USGS gage stations for the period in which the water quality data was collected using the matched gage station is representative of the flow condition at the impaired reach of the Mississippi River and Joachim Creek.

- The 25th percentile water hardness value (193 mg/L) was used to calculate the WQS for both lead and zinc and is representative of the hardness conditions found at the impaired water bodies.

- Chronic WQS values for both lead and zinc are protective of short-term (acute) exposures as well for both metals. This assumption was adopted largely because contaminated sediments, representing a long-term source and sink for these metals, resist short-term flux and thus the chronic WQS would be most appropriate for both metals.

- EqP calculations estimating porewater concentrations from bulk sediment were used to confirm the general nature of the impairment expressed as in-stream, aqueous phase concentrations.

- Measured concentrations assumed to be one-half the method detection limit when not detected.

As documented previously in this TMDL, the load duration curve method was used to calculate pollutant-specific TMDLs for Mississippi River and Joachim Creek. Because the load duration curve method relies on measured water quality data, regional water hardness data, and a wide range of “flow exceedance” data, it represents a complete range of flows and pollutant loads anticipated in these water bodies. However, the lack of water quality data at high stream flows did not allow for calculation of pollutant load reductions at these flow conditions. These data would have been beneficial to include in the analysis since the majority of dissolved metals and sediment loading can be expected to be contributed during high stream flow conditions. As result, there is some uncertainty as to the actual pollutant reductions necessary to achieve water quality standards during these stream conditions.

8. Seasonal Variation

Federal regulations at 40 CFR §130.7(c)(1) require TMDLs take into consideration seasonal variation in applicable standards. Although there were insufficient water quality data to determine any seasonal pattern that may be occurring in the Mississippi River watershed, the use of flow and load duration curves represents the allowable pollutant load under variable flow conditions across all seasons. The results obtained using the load duration curve method are therefore more robust and reliable over all flows and seasons when compared with those obtained under more limited conditions (e.g., critical low flow conditions).

9. Monitoring Plans

The Department has not yet developed a formal monitoring plan for this water body. Post-TMDL monitoring is usually scheduled and carried out by the department approximately three years after the approval of the TMDL or in a reasonable time period following completion of permit compliance schedules and the application of new effluent limits. Additionally, any available volunteer water quality monitoring or permittee instream monitoring that occurs on Mississippi River or Joachim Creek will be used for screening purposes to compare the stream's current condition with future, post-TMDL conditions. The department will also routinely examine any physical habitat, water quality, invertebrate community, and fish community data that may be collected from these streams by the Missouri Department of Conservation under its Resource Assessment and Monitoring Program. This program randomly samples streams across Missouri on a five to six year rotating schedule.

10. Implementation Plans

The water quality impairment for Mississippi River is lead and zinc in sediment from the Doe Run Herculaneum Smelter. Nonpoint source contributions of these pollutants are expected to be minor. Therefore, any practices used to implement this TMDL will primarily focus on point source contributions.

10.1 Point Sources

This part of the TMDL will be implemented through permit action. Effluent limits and monitoring requirements for the Doe Run Herculaneum Smelter operating permit will be reevaluated to reflect the water quality targets set by the TMDL as the permit is renewed. This includes effluent limits for lead and zinc using the wasteload allocations developed for this TMDL. Future inspections of the Doe Run Herculaneum Smelter facility by the department will also determine the extent and nature of erosion at the site. Discharge permits may need to be amended to include additional measures (e.g., a storm water pollution prevention plan) that ensure the facility does not continue to cause or contribute to the impairment of Mississippi River.

An Administrative Order on Consent (AOC) for the Herculaneum Smelter was made final in May 2001. This AOC, and its three subsequent modifications, outline many actions Doe Run is required to take to prevent metals contamination from leaving the smelter site. One focus is preventing metals contamination of surface water and sediment in both Joachim Creek and the Mississippi River. The November 2003 Alternatives Evaluation Report (similar in scope and purpose to an Environmental Evaluation/Cost Analysis), presented possible alternative actions to control the waste material on the slag pile.

On October 5, 2002, EPA issued an Action Memorandum, which selected the removal action to be implemented for the slag storage area. The selected removal action consists of engineering measures to contain and treat stormwater runoff; control wind and water erosion; prevent direct contact other than by employees or contractors of Doe Run; provide for flood protection, long-term stability and mitigation of wetlands disturbance. This remedial action includes the construction of a flood protection berm, a storm water retention basin and an engineered cover for the slag material following grading work. Work continues on these and other response activities and, currently (Summer 2010), work on the slag pile berm has been delayed due to flooding.

Additionally, any other facilities identified as contributing to the metals contaminated sediment loading of the impaired segment must adopt appropriate best management practices to reduce such loading from their outfalls. Best management practices are recommended methods, structures, and practices designed to prevent or reduce water pollution. These facilities must also regularly measure instream pollutant concentrations to determine the efficacy of the control measures.

10.2 Nonpoint Sources

Nonpoint source reductions are currently not necessary to reduce pollutant loading of lead and zinc to the impaired portion of the Mississippi River. Reductions obtained by implementing the wasteload allocations found in this TMDL should restore water quality in Mississippi River. However, best management practices currently employed within the watershed must continue to be implemented to ensure antidegradation requirements are met. Further nonpoint source reductions in the watershed may be implemented through best management practices funded wholly or in part by Section 319 grants[10] or AgNPS SALT Program projects[11]. The department may also work with the Natural Resources Conservation Service and the local Soil and Water Conservation District to encourage area landowners to implement best management practices.

11. Reasonable Assurances

The Department of Natural Resources has the authority to issue and enforce Missouri State Operating Permits. Inclusion of effluent limits determined from the wasteload allocations established by the TMDL into a state permit, along with effluent monitoring reported to the department, should provide a reasonable assurance that in-stream water quality standards will be met. In most cases, "Reasonable Assurance" in reference to TMDLs relates only to point sources. As a result, any assurances that nonpoint source contributors of nutrients will implement measures to reduce their contribution in the future will not be found in this section. Instead, discussion of reduction efforts relating to nonpoint sources can be found in the "Implementation" section of this TMDL.

12. Public Participation

The Mississippi River is included on the approved 2008 Missouri 303(d) List of impaired waters. EPA regulations at 40 CFR 130.7(c)(1) require that TMDLs be subject to public review. The public notice period for the draft Mississippi River TMDL was July 30, 2010 to September 13, 2010. Groups receiving the public notice announcement included the Missouri Clean Water Commission,

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[10] Under section 319, State, Territories and Indian Tribes receive grant money that support a wide variety of activities including technical assistance, financial assistance, education, training, technology transfer, demonstration projects and monitoring to assess the success of specific nonpoint source implementation projects.

[11] Program that allows county soil and water conservation districts (SWCD) to direct technical and financial assistance to landowners with land identified and prioritized as having water quality impairments that address agricultural nonpoint source pollution problems.

the Water Quality Coordinating Committee, Doe Run Resources Corporation, Jefferson County Commissioners, 48 Stream Team volunteers in the watershed and the two state legislators representing Jefferson County. Announcement of the public notice period for this TMDL was also issued as a press release to local media outlets in the proximity of the Mississippi River – Joachim Creek watershed. Finally, the public notice, the TMDL Information Sheet, and this document were placed on the department website, making them available to anyone with Internet access. One comment was received on September 13, 2010 and will be placed in the Mississippi River docket [file] along with the department's response and any other documentation.

13. Administrative Record and Supporting Documentation

An administrative record on the Mississippi River TMDL has been assembled and is being kept on file with department. It includes the following:

- Herculaneum Smelter (The Doe Run Resources Corporation) permit #MO-0000281.
- Administrative Order on Consent for The Doe Run Resources Corporation, Docket No. RCRA7-2000-0018, CERCLA-7-2000-0029, signed November 29, 2001.
- Engineering Evaluation/Cost analysis Report, Herculaneum Smelter, Herculaneum, Missouri, May 2004, Revised November 2005.
- Administrative Order on Consent for The Doe Run Resources Corporation, Docket No. RCRA7-2000-0018, CERCLA-7-2000-0029, Third Modification [contains the chosen alternative], signed July 24, 2006.
- Mississippi River data.
- Flow data and calculations.
- Public notice announcement.
- Mississippi River Information Sheet.

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Appendices

Appendix A – Summary of Discharge Monitoring Report Data, Herculaneum Smelter (MO-0000281) Outfalls #001 and #003

Appendix B – Summary of Flow Data for Mississippi River and Joachim Creek

Appendix C – Mississippi River and Joachim Creek Lead and Zinc TMDLs and Wasteload Allocations

Appendix A – Summary of Discharge Monitoring Report Data, Herculaneum Smelter (MO-0000281) Outfalls #001 and #003

Outfall	Maximum Measured Flow (mgd)	Monitoring Period End Date	Maximum Total Concentration (µg/L)		Estimated Dissolved Concentration (µg/L)*	
			Pb	Zn	Pb	Zn
001	0.59	12/31/2003	20.0	160.0	13.9	157.8
001	0.77	1/31/2004	40.0	260.0	27.8	256.4
001	0.788	2/29/2004	30.0	120.0	20.9	118.3
001	0.725	3/31/2004	90.0	159.0	62.6	156.8
001	0.769	4/30/2004	20.0	50.0	13.9	49.3
001	0.556	5/31/2004	160.0	1540.0	111.2	1518.4
001	0.196	6/30/2004	170.0	1040.0	118.2	1025.4
001	0.449	7/31/2004	80.0	730.0	55.6	719.8
001	0.573	8/31/2004	20.0	20.0	13.9	19.7
001	0.498	9/30/2004	37.5	410.0	26.1	404.3
001	0.502	10/31/2004	20.0	840.0	13.9	828.2
001	0.52	11/30/2004	60.0	420.0	41.7	414.1
001	0.425	12/31/2004	150.0	1420.0	104.3	1400.1
001	0.53	1/31/2005	1210.0	2770.0	841.0	2731.2
001	0.354	2/28/2005	20.0	70.0	13.9	69.0
001	0.539	3/31/2005	80.0	140.0	55.6	138.0
001	0.647	4/30/2005	50.0	50.0	34.8	49.3
001	0.554	5/31/2005	60.0	230.0	41.7	226.8
001	0.61	6/30/2005	130.0	110.0	90.4	108.5
001	0.573	7/31/2005	100.0	50.0	69.5	49.3
001	NA	8/31/2005	90.0	450.0	62.6	443.7
001	NA	9/30/2005	100.0	410.0	69.5	404.3
001	NA	10/31/2005	70.0	70.0	48.7	69.0
001	0.521	11/30/2005	110.0	260.0	76.5	256.4
001	0.521	12/31/2005	150.0	1600.0	104.3	1577.6
001	0.3	1/31/2006	40.0	310.0	27.8	305.7
001	0.409	2/28/2006	50.0	260.0	34.8	256.4
001	0.479	4/30/2006	40.0	150.0	27.8	147.9
001	0.791	5/31/2006	140.0	60.0	97.3	59.2
003	1.496	1/31/2001	220.0	16.0	152.9	15.8
003	1.765	2/28/2001	5.0	2.5	3.5	2.5
003	1.709	3/31/2001	5.0	6.0	3.5	5.9
003	1.708	4/30/2001	5.0	2.5	3.5	2.5
003	1.683	5/31/2001	5.0	5.0	3.5	4.9
003	1.633	6/30/2001	10.0	6.0	7.0	5.9
003	1.78	7/31/2001	30.0	33.0	20.9	32.5
003	2.089	8/31/2001	5.0	9.0	3.5	8.9
003	1.635	9/30/2001	60.0	13.0	41.7	12.8
003	1.86	10/31/2001	90.0	7.0	62.6	6.9
003	1.79	11/30/2001	5.0	8.0	3.5	7.9

Outfall	**Maximum Measured Flow (mgd)**	**Monitoring Period End Date**	**Maximum Total Concentration (µg/L)**		**Estimated Dissolved Concentration (µg/L)***	
			Pb	**Zn**	**Pb**	**Zn**
003	2.083	12/31/2001	5.0	2.5	3.5	2.5
003	1.53	1/31/2002	5.0	2.5	3.5	2.5
003	1.475	2/28/2002	5.0	2.5	3.5	2.5
003	1.67	3/31/2002	5.0	2.5	3.5	2.5
003	1.8	4/30/2002	5.0	2.5	3.5	2.5
003	3.07	5/31/2002	5.0	2.5	3.5	2.5
003	2.248	6/30/2002	40.0	29.0	27.8	28.6
003	2.36	7/31/2002	5.0	7.0	3.5	6.9
003	1.554	8/31/2002	5.0	2.5	3.5	2.5
003	1.3	9/30/2002	5.0	2.5	3.5	2.5
003	1.676	10/31/2002	20.0	2.5	13.9	2.5
003	1.183	11/30/2002	5.0	6.0	3.5	5.9
003	2.003	12/31/2002	20.0	2.5	13.9	2.5
003	1.305	1/31/2003	0.0	0.0	0.0	0.0
003	1.026	2/28/2003	0.0	0.0	0.0	0.0
003	1.18	3/31/2003	0.0	0.0	0.0	0.0
003	1.234	4/30/2003	40.0	40.0	27.8	39.4
003	1.256	5/31/2003	0.0	0.0	0.0	0.0
003	0.1541	6/30/2003	20.0	60.0	13.9	59.2
003	1.819	7/31/2003	20.0	20.0	13.9	19.7
003	2.098	8/31/2003	20.0	30.0	13.9	29.6
003	1.59	9/30/2003	0.0	0.0	0.0	0.0
003	1.225	10/31/2003	0.0	0.0	0.0	0.0
003	1.038	11/30/2003	0.0	0.0	0.0	0.0
003	1.208	12/31/2003	0.0	0.0	0.0	0.0
003	2	1/31/2004	160.0	30.0	111.2	29.6
003	1.671	2/29/2004	0.0	0.0	0.0	0.0
003	1.389	3/31/2004	0.0	0.0	0.0	0.0
003	1.871	4/30/2004	NA	NA	NA	NA
003	1.566	5/31/2004	20.0	NA	13.9	NA
003	1.347	6/30/2004	0.0	0.0	0.0	0.0
003	1.691	7/31/2004	20.0	0.0	13.9	0.0
003	1.876	8/31/2004	0.0	0.0	0.0	0.0
003	0.826	9/30/2004	0.0	0.0	0.0	0.0
003	1.154	10/31/2004	130.0	30.0	90.4	29.6
003	2.638	11/30/2004	0.0	0.0	0.0	0.0
003	2.101	12/31/2004	20.0	20.0	13.9	19.7
003	1.277	2/28/2005	10.0	0.0	7.0	0.0
003	1.148	3/31/2005	20.0	0.014U	13.9	0.014U
003	1.522	4/30/2005	0.0	0.0	0.0	0.0
003	1.318	5/31/2005	70.0	40.0	48.7	39.4
003	1.691	6/30/2005	310.0	60.0	215.5	59.2
003	1.324	7/31/2005	180.0	40.0	125.1	39.4

Outfall	**Maximum Measured Flow (mgd)**	**Monitoring Period End Date**	**Maximum Total Concentration (µg/L)**		**Estimated Dissolved Concentration (µg/L)***	
			Pb	**Zn**	**Pb**	**Zn**
003	NA	8/31/2005	30.0	0.0	20.9	0.0
003	NA	9/30/2005	40.0	0.0	27.8	0.0
003	NA	10/31/2005	50.0	10.0	34.8	9.9
003	2.5	11/30/2005	40.0	0.0	27.8	0.0
003	1.632	1/31/2006	10.0	10.0	7.0	9.9
003	1.916	2/28/2006	10.0	0.0	7.0	0.0
003	2.515	4/30/2006	0.0	10.0	0.0	9.9
003	1.993	5/31/2006	0.0	0.0	0.0	0.0

Note: NA indicates not available

mgd = million gallons per day, µg/L = micrograms per liter

* estimated using EPA (1996) chronic freshwater criteria conversion factors for dissolved metals (Pb = 0.695 and Zn = 0.986)

Appendix B – Summary of Flow Data for Mississippi River and Joachim Creek

	Flow (cubic feet per second)	
P	USGS 07010000 Mississippi River at St. Louis, MO	USGS 07019570 Joachim Creek at Hematite, MO*
0.1	970576	1606
0.2	898608	1296
0.3	855100	1162
0.4	788912	1028
0.5	754520	913
0.6	736184	824
0.7	726516	783
0.8	702216	738
0.9	689092	662
1	675640	620
2	586520	357
3	528920	253
4	497000	201
5	480000	167
6	459000	146
7	437000	127
8	422000	114
9	408920	104
10	395800	95.9
11	386000	88.5
12	376000	83.0
13	367000	76.9
14	356000	72.5
15	345000	68.7
16	336080	65.0
17	326000	61.6
18	314000	58.5
19	305000	56.1
20	297000	53.8
21	289000	51.3
22	282000	49.4
23	276000	47.4
24	269000	45.6
25	262000	44.0
26	256000	42.4
27	250000	40.8
28	245640	39.3
29	241000	37.9
30	236000	36.5
31	232000	35.3
32	228000	34.1
33	224000	33.0
34	221000	31.9

	Flow (cubic feet per second)	
P	USGS 07010000 Mississippi River at St. Louis, MO	USGS 07019570 Joachim Creek at Hematite, MO*
35	218000	31.0
36	214000	29.9
37	211000	28.9
38	208000	28.0
39	204000	27.1
40	200000	26.3
41	196000	25.4
42	192000	24.6
43	189000	23.8
44	185000	23.0
45	182000	22.2
46	179000	21.5
47	176000	20.8
48	173240	20.1
49	171000	19.5
50	168000	18.8
51	166000	18.1
52	164000	17.6
53	161000	16.9
54	159000	16.3
55	157000	15.8
56	155000	15.4
57	153000	14.8
58	151000	14.4
59	149000	14.0
60	147000	13.5
61	145000	13.1
62	143000	12.8
63	141000	12.4
64	139000	12.0
65	136000	11.7
66	134000	11.4
67	133000	11.0
68	131000	10.7
69	129000	10.3
70	128000	10.0
71	126000	9.7
72	124000	9.4
73	123000	9.1
74	121000	8.8
75	119000	8.6
76	117000	8.3
77	116000	8.0
78	114000	7.8
79	112000	7.6
80	110000	7.4

	Flow (cubic feet per second)	
P	USGS 07010000 Mississippi River at St. Louis, MO	USGS 07019570 Joachim Creek at Hematite, MO*
81	108000	7.1
82	106000	6.9
83	104000	6.7
84	102000	6.4
85	99800	6.2
86	97568	6.0
87	94400	5.8
88	91544	5.6
89	89200	5.4
90	87000	5.1
91	84208	5.0
92	81096	4.7
93	78000	4.4
94	75900	4.3
95	73600	3.9
96	71148	3.6
97	68500	3.2
98	65424	2.5
99	60400	1.62
99.1	59982	1.55
99.2	59339	1.39
99.3	58848	1.24
99.4	58009	1.14
99.5	56224	0.95
99.6	53970	0.86
99.7	50618	0.55
99.8	44985	0.24
99.9	42821	0.20

* Note: Flows are estimated using equation derived from flow regression analysis for USGS 07019570 Joachim Creek at Hematite, MO and USGS 07018100 Big River at Richwoods, MO.

Appendix C – Mississippi River and Joachim Creek Lead and Zinc TMDLs and Wasteload Allocations

Percentile flow (P)	Pb TMDL (lb/day)		Zinc TMDL (lb/day)		Pb WLA (lb/day)		Zinc WLA (lb/day)	
	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek
0.1	28437	47.05	1025963	1697.55	28437	47.05	1025957	1697.55
0.2	26328	37.98	949888	1370.42	26328	37.98	949882	1370.42
0.3	25053	34.06	903897	1228.79	25053	34.06	903891	1228.79
0.4	23114	30.11	833932	1086.19	23114	30.11	833926	1086.19
0.5	22107	26.75	797577	965.21	22106	26.75	797571	965.21
0.6	21569	24.15	778195	871.33	21569	24.15	778189	871.33
0.7	21286	22.93	767975	827.45	21286	22.93	767969	827.45
0.8	20574	21.62	742288	780.00	20574	21.62	742283	780.00
0.9	20190	19.40	728416	699.86	20189	19.40	728410	699.86
1	19795	18.18	714196	655.82	19795	18.18	714190	655.82
2	17184	10.47	619990	377.66	17184	10.47	619984	377.66
3	15497	7.416	559103	267.55	15497	7.416	559097	267.55
4	14562	5.875	525362	211.96	14561	5.875	525356	211.96
5	14063	4.890	507392	176.41	14063	4.890	507386	176.41
6	13448	4.264	485193	153.83	13448	4.264	485187	153.83
7	12804	3.727	461938	134.47	12803	3.727	461932	134.47
8	12364	3.347	446082	120.76	12364	3.347	446076	120.76
9	11981	3.057	432255	110.28	11981	3.057	432249	110.28
10	11596	2.811	418387	101.40	11596	2.811	418381	101.40
11	11309	2.593	408027	93.54	11309	2.593	408022	93.54
12	11016	2.431	397457	87.69	11016	2.431	397451	87.69
13	10753	2.254	387943	81.31	10753	2.254	387937	81.31
14	10430	2.125	376315	76.68	10430	2.125	376310	76.68
15	10108	2.013	364688	72.61	10108	2.013	364682	72.61
16	9847	1.905	355259	68.74	9847	1.905	355253	68.74
17	9551	1.805	344603	65.11	9551	1.805	344598	65.11
18	9200	1.713	331919	61.79	9200	1.713	331913	61.79
19	8936	1.644	322405	59.30	8936	1.644	322399	59.30
20	8702	1.577	313949	56.88	8702	1.577	313943	56.88
21	8467	1.503	305492	54.22	8467	1.503	305486	54.22
22	8262	1.447	298093	52.20	8262	1.447	298087	52.20

Percentile flow (P)	Pb TMDL (lb/day)		Zinc TMDL (lb/day)		Pb WLA (lb/day)		Zinc WLA (lb/day)	
	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek
23	8086	1.389	291750	50.11	8086	1.389	291744	50.11
24	7881	1.335	284351	48.17	7881	1.335	284345	48.17
25	7676	1.289	276951	46.49	7676	1.289	276945	46.49
26	7501	1.241	270609	44.78	7500	1.241	270603	44.78
27	7325	1.194	264266	43.09	7325	1.194	264261	43.09
28	7197	1.152	259658	41.55	7197	1.152	259652	41.55
29	7061	1.110	254753	40.06	7061	1.110	254747	40.06
30	6915	1.069	249468	38.57	6914	1.069	249462	38.57
31	6797	1.036	245239	37.36	6797	1.036	245233	37.36
32	6680	1.000	241011	36.07	6680	1.000	241005	36.07
33	6563	0.966	236783	34.86	6563	0.966	236777	34.86
34	6475	0.935	233612	33.74	6475	0.935	233606	33.74
35	6387	0.908	230440	32.76	6387	0.908	230434	32.76
36	6270	0.877	226212	31.64	6270	0.877	226206	31.64
37	6182	0.848	223041	30.59	6182	0.848	223035	30.59
38	6094	0.821	219870	29.62	6094	0.821	219864	29.62
39	5977	0.794	215641	28.65	5977	0.794	215636	28.65
40	5860	0.770	211413	27.77	5860	0.770	211407	27.77
41	5743	0.745	207185	26.88	5742	0.745	207179	26.88
42	5625	0.720	202957	25.99	5625	0.720	202951	25.99
43	5537	0.698	199785	25.17	5537	0.698	199780	25.17
44	5420	0.673	195557	24.30	5420	0.673	195551	24.30
45	5332	0.651	192386	23.49	5332	0.651	192380	23.49
46	5244	0.631	189215	22.76	5244	0.631	189209	22.76
47	5157	0.609	186044	21.96	5156	0.609	186038	21.96
48	5076	0.589	183126	21.26	5076	0.589	183120	21.26
49	5010	0.571	180758	20.59	5010	0.571	180752	20.59
50	4922	0.551	177587	19.86	4922	0.551	177581	19.86
51	4864	0.530	175473	19.14	4863	0.530	175467	19.14
52	4805	0.515	173359	18.57	4805	0.515	173353	18.57
53	4717	0.495	170188	17.85	4717	0.495	170182	17.85
54	4659	0.479	168073	17.28	4658	0.479	168068	17.28
55	4600	0.463	165959	16.72	4600	0.463	165953	16.72

Percentile flow (P)	**Pb TMDL (lb/day)**		**Zinc TMDL (lb/day)**		**Pb WLA (lb/day)**		**Zinc WLA (lb/day)**	
	Mississippi River	**Joachim Creek**	**Mississippi River**	**Joachim Creek**	**Mississippi River**	**Joachim Creek**	**Mississippi River**	**Joachim Creek**
56	4541	0.450	163845	16.23	4541	0.450	163839	16.23
57	4483	0.435	161731	15.68	4483	0.435	161725	15.68
58	4424	0.421	159617	15.18	4424	0.421	159611	15.18
59	4366	0.410	157503	14.78	4365	0.410	157497	14.78
60	4307	0.396	155389	14.30	4307	0.396	155383	14.30
61	4248	0.385	153275	13.89	4248	0.385	153269	13.89
62	4190	0.374	151160	13.49	4190	0.374	151155	13.49
63	4131	0.363	149046	13.09	4131	0.363	149040	13.09
64	4073	0.352	146932	12.68	4072	0.352	146926	12.68
65	3985	0.343	143761	12.36	3984	0.343	143755	12.36
66	3926	0.334	141647	12.04	3926	0.334	141641	12.04
67	3897	0.323	140590	11.64	3897	0.323	140584	11.64
68	3838	0.314	138476	11.31	3838	0.314	138470	11.31
69	3780	0.302	136361	10.91	3779	0.302	136356	10.91
70	3750	0.293	135304	10.59	3750	0.293	135299	10.59
71	3692	0.285	133190	10.26	3691	0.285	133184	10.26
72	3633	0.274	131076	9.90	3633	0.274	131070	9.90
73	3604	0.267	130019	9.62	3604	0.267	130013	9.62
74	3545	0.258	127905	9.30	3545	0.258	127899	9.30
75	3487	0.251	125791	9.06	3486	0.251	125785	9.06
76	3428	0.242	123677	8.73	3428	0.242	123671	8.73
77	3399	0.235	122620	8.49	3399	0.235	122614	8.49
78	3340	0.229	120505	8.25	3340	0.229	120500	8.25
79	3281	0.223	118391	8.05	3281	0.223	118386	8.05
80	3223	0.216	116277	7.78	3223	0.216	116271	7.78
81	3164	0.209	114163	7.52	3164	0.209	114157	7.52
82	3106	0.202	112049	7.28	3106	0.202	112043	7.28
83	3047	0.195	109935	7.04	3047	0.195	109929	7.04
84	2988	0.188	107821	6.80	2988	0.188	107815	6.80
85	2924	0.182	105495	6.55	2924	0.182	105489	6.55
86	2859	0.177	103136	6.39	2858	0.177	103130	6.39
87	2766	0.171	99787	6.15	2766	0.171	99781	6.15
88	2682	0.164	96768	5.91	2682	0.164	96762	5.91

Percentile flow (P)	Pb TMDL (lb/day)		Zinc TMDL (lb/day)		Pb WLA (lb/day)		Zinc WLA (lb/day)	
	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek	Mississippi River	Joachim Creek
89	2613	0.157	94290	5.67	2613	0.157	94284	5.67
90	2549	0.150	91965	5.43	2549	0.150	91959	5.43
91	2467	0.146	89013	5.26	2467	0.146	89008	5.26
92	2376	0.138	85724	4.96	2376	0.138	85718	4.96
93	2285	0.130	82451	4.70	2285	0.130	82445	4.70
94	2224	0.126	80231	4.54	2224	0.126	80225	4.54
95	2156	0.115	77800	4.14	2156	0.115	77794	4.14
96	2085	0.106	75208	3.81	2084	0.106	75202	3.81
97	2007	0.094	72409	3.41	2007	0.094	72403	3.41
98	1917	0.072	69157	2.60	1917	0.072	69152	2.60
99	1770	0.048	63847	1.72	1769	0.048	63841	1.72
99.1	1757	0.045	63404	1.63	1757	0.045	63399	1.63
99.2	1739	0.041	62725	1.47	1738	0.041	62720	1.47
99.3	1724	0.036	62207	1.31	1724	0.036	62201	1.31
99.4	1700	0.033	61319	1.20	1699	0.033	61313	1.20
99.5	1647	0.028	59432	1.01	1647	0.028	59427	1.01
99.6	1581	0.025	57049	0.91	1581	0.025	57044	0.91
99.7	1483	0.016	53507	0.59	1483	0.016	53501	0.59
99.8	1318	0.007	47552	0.25	1318	0.007	47546	0.25
99.9	1255	0.006	45265	0.21	1254	0.006	45259	0.21