EPA Region 7 TMDL Review

TMDL ID: MO_1707 **State:** MO

Document Name: MISSISSIPPI RIVER

Basin(s): UPPER MISSISSIPPI-MERAMEC (CAHOKIA-JOACHIM RIVER BASIN)
HUC(s): 07140101, 07140105, 7140101
Water body(ies): MISSISSIPPI R., MISSISSIPPI RIVER
Tributary(ies): JOACHIM CREEK
Pollutant(s): LEAD, LEAD (SEDIMENT), ZINC, ZINC (SEDIMENT)

Submittal Date: 11/8/2010 **Approved:** Yes

Submittal Letter

State submittal letter indicates final Total Maximum Daily Load(s) (TMDL) for specific pollutant(s)/water(s) were adopted by the state, and submitted to EPA for approval under section 303(d) of the Clean Water Act [40 CFR § 130.7(c)(1)]. Include date submitted letter was received by EPA, date of receipt of any revisions, and the date of original approval if submittal is a phase II TMDL.

This TMDL document was formally submitted by the Missouri Department of Natural Resources (MDNR). The United States Environmental Protection Agency (EPA) received this TMDL document by mail on November 8, 2010. A revision to this document was received by email on November 30, 2010.

Water Quality Standards Attainment

The water body's loading capacity (LC) for the applicable pollutant is identified and the rationale for the method used to establish the cause-and-effect relationship between the numeric target and the identified pollutant sources is described. TMDL and associated allocations are set at levels adequate to result in attainment of applicable water quality standards (WQS) [40 CFR § 130.7(c)(1)]. A statement that WQS will be attained is made.

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 Herculaneum lead (Pb) smelter, which has been active since 1892, is located near Joachim Creek at Herculaneum in Jefferson County. Approximately 70 percent of the United States' primary Pb supply comes from eight mines in southern Missouri, and the Herculaneum smelter constitutes the principal source of refined Pb. This smelter has been found to contribute heavy metals to the aquatic system via means of wastewater discharges, erosion of slag piles, concentrate transportation and handling, air emission fallout and fugitive emissions. As a result, this water quality limited segment near Herculaneum in Jefferson County is included on the EPA-approved 2008 Missouri 303(d) List of impaired waters with the pollutants of concern being Pb and zinc (Zn).

MDNR does not have numerical guidance or criteria developed for Pb and Zn in freshwater sediment. However, sediment data has been typically collected from the Mississippi River within the segment of interest and its tributary, Joachim Creek. Levels of Pb and Zn reported in some of these sediment samples are in excess of the values commonly reported as toxic to aquatic life, consensus based threshold and probable effect concentrations as suggested by MacDonald et al (2000). Because the majority of toxicity from these metals occurs in pore water in the aquatic environment, it is important to know their pore-water concentrations. An equilibrium partitioning method was applied to estimate the pore-water and its overlaying instream concentrations. Chronic Pb (5.1

micrograms per liter (µg/L)) and Zn (186.8 µg/L) criteria were used as the instream standards, which were calculated using the 25th percentile of hardness value (193 milligram calcium carbonate (mg $CaCO_3$) /L). The TMDLs for dissolved Pb and Zn were determined using load duration curves (LDCs). The LCs at the 50 percent flow exceedance, for the Mississippi River and Joachim Creek are 4,922 pounds per day (lb/day) and 0.551 lb/day for dissolved Pb, and 177,587 lb/day and 19.86 lb/day for dissolved Zn, respectively.

EPA believes that the reductions in instream dissolved Pb and Zn loads protects the warm water aquatic life and human health uses of the stream and these TMDLs should result in WQS attainment.

Numeric Target(s)

Submittal describes applicable WQS, including beneficial uses, applicable numeric and/or narrative criteria. If the TMDL is based on a target other than a numeric water quality criterion, then a numeric expression, site specific if possible, was developed from a narrative criterion and a description of the process used to derive the target is included in the submittal.

The Mississippi River has multiple beneficial uses, therefore, it is necessary to evaluate the protectiveness of Pb and Zn human health criteria as well as criteria for the protection of aquatic life. Because elevated Pb and Zn concentrations were consistently found in the sediment associated with the Doe Run Herculaneum Smelter and aquatic life exposures to these metals are considered chronic in nature. Chronic aquatic life protection criteria (see the following table) are used in this TMDL, which are also adequately protective of human health from consumption of contaminated fish. The impaired segment is given High Priority for TMDL development on the State's 303(d) List.

Segment ID	Designated Uses	Impaired Use	TMDL Endpoint
Mississippi River (1707)	Warm Water Aquatic Life, Human Health (Fish Consumption), Drinking Water Supply, Industrial, Irrigation, Livestock and Wildlife Watering, Whole Body Contact Recreation (Category B), Secondary Contact Recreation	Warm Water Aquatic Life Human Health (Fish Consumption)	Dissolved Pb 5.1 µg/L Dissolved Zn 186.8 µg/L

The TMDL endpoints are calculated from the following equations.

Chronic dissolved Pb $= e^{(1.273*\ln(\text{Hardness})-4.7047)}*(1.46203-\ln((\text{Hardness})*0.145712))$

Chronic dissolved Zn $= e^{(0.8473*\ln(\text{Hardness})+0.785271)}*0.986$

In the absence of measured hardness data from the impaired reach of the Mississippi River, these water quality criteria were calculated using the 25th percentile hardness value of 193 mg $CaCO_3$ /L obtained from water quality data collected at Station 1707/162.5.

Because of the lack of measured instream water quality data and the state's sediment standards, the threshold effect concentrations for Pb (35.8 milligrams per kilogram (mg/kg)) and Zn (121 mg/kg) are used as the secondary TMDL targets to additionally protect warm water aquatic life and human health from the impairment. All sediment samples collected in Joachim Creek exceeded either applicable Pb or Zn threshold effect concentrations, chronic instream criteria, or both. Since the metal loadings from Joachim Creek significantly causes and contributes to elevated sediment Pb and Zn concentrations downstream of its confluence with the Mississippi River, Joachim Creek is included in the TMDL analysis for Mississippi River to account for its contribution to the impairment.

Pollutant(s) of concern

An explanation and analytical basis for expressing the TMDL through surrogate measures (e.g., parameters such as percent fines and turbidity for sediment impairments, or chlorophyll-a and phosphorus loadings for excess algae) is provided, if applicable. For each identified pollutant, the submittal describes analytical basis for conclusions, allocations and margin of safety (MOS) that do not exceed the LC. If submittal is a phase II TMDL there are refined relationships linking the load to WQS attainment. If there is an increase in the TMDL there is a refined relationship specified to validate the increase in TMDL (either load allocation (LA) or waste load allocation (WLA)). This section will compare and validate the change in targeted load between the versions.

Levels of Pb and Zn reported in some of the sediment samples collected from Mississippi River and Joachim Creek are in excess of the values commonly reported as toxic to aquatic life, consensus based threshold and probable effect concentrations. The threshold and probable effect concentrations are the concentration below which adverse effects are not expected to occur and the concentration above which adverse effects are likely to appear, respectively. The highest Pb value measured in sediment was 26,400 mg/kg at the smelter storm water outfall in Joachim Creek sampled October 2001. The highest Zn concentration was 5,440 mg/kg and was collected at the same location and on the same date. The 1995 data collected by the U.S. Fish and Wildlife Service also indicated that Pb in sediment were 37 mg/kg, 7,720 mg/kg, 7,590 mg/kg and 23 mg/kg, which are all above the threshold effect concentration (35.8 mg/kg), and two of these values are above the probable effect concentration of 128 mg/kg. The four reported values for Zn 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 (121 mg/kg), and the same two values are also above the probable effect concentration of 459 mg/kg. Although the TMDL is not based on fish tissue data, high levels of Pb in fish tissue have been reported.

Chronic Pb (5.1 µg/L) and Zn (186.8 µg/L) targets are set to address the pollutants causing the impairment. Based on sediment samples collected in Mississippi River and Joachim Creek, the linkage of Pb and Zn impairment to Doe Run Herculaneum Smelter is direct. The wastewater from this facility and its associated sources (e.g., slag piles) is attributable to the impairment seen in the 5-mile reach of Mississippi River. Because of the absence of measured water quality (or instream) data and the state's sediment standards, pore water concentrations were estimated for instream Pb and Zn, based on the threshold effect concentrations for Pb (35.8 mg/kg) and Zn (121 mg/kg), to evaluate the impairment for this TMDL.

LA was analyzed but not targeted by this TMDL because the Pb and Zn impairment is triggered by the Doe Run Herculaneum Smelter.

Source Analysis

Important assumptions made in developing the TMDL, such as assumed distribution of land use in the watershed, population characteristics, wildlife resources, and other relevant information affecting the characterization of the pollutant of concern and its allocation to sources, are described. Point, nonpoint and background sources of pollutants of concern are described, including magnitude and location of the sources. Submittal demonstrates all significant sources have been considered. If this is a phase II TMDL any new sources or removed sources will be specified and explained.

The only known permitted point source in the watershed is the Doe Run Herculaneum Smelter (MO0000281). It has five outfalls, four of which discharge into the Mississippi River and one into Joachim Creek. The Herculaneum Smelter has been listed as the cause of the dissolved Pb and Zn impairment in the Mississippi River. Analysis of the Pb and Zn in sediment data 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 the highest in Joachim Creek in the area around Outfall #004. 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 another possible source of Pb and Zn contamination. Other areas of Joachim Creek adjacent to the Herculaneum facility also exhibit elevated levels of Pb and Zn in sediment, although not as great as the area below the slag storage area. Air deposition from the Herculaneum smelter is another source of Pb and Zn. Lead and Zn 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 Pb and Zn 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 Pb and Zn to the impaired segment.

Forest and grassland are the dominant land uses, which are comprised of approximately 63 and 28 percent of the Mississippi River watershed, respectively. Cropland occupies 2 percent of the watershed. Urban development accounts for about 5 percent of the land use area. Likewise, forest and grassland account for 73 percent of Joachim Creek watershed while urban development constitutes about 12 percent of the total area. As compared to the Herculaneum Smelter and its associated areas (i.e., Herculaneum slag pile), nonpoint source loading of dissolved Pb and Zn from these rural areas is not significant. Although urban storm water may contribute the metal loadings from roads, highways and parking lots that contain tire residues, exhaust fumes, battery fluid and motor oil, its contribution to the impairment is very minor.

All known sources of dissolved Pb and Zn have been considered in this TMDL.

Allocation - Loading Capacity

Submittal identifies appropriate WLA for point, and load allocations for nonpoint sources. If no point sources are present the WLA is stated as zero. If no nonpoint sources are present, the LA is stated as zero [40 CFR § 130.2 (i)]. If this is a phase II TMDL the change in LC will be documented in this section.

Dissolved Pb and Zn LDCs were developed for both the Mississippi River and Joachim Creek to identify their LCs at all flows. For this TMDL, LA is set to zero lb/day, with margin of safety being implicit. The entire LCs are given to WLAs because the Doe Run Herculaneum Smelter (MO0000281) and its related sources are clearly responsible for dissolved Pb and Zn excursions based on sediment data using an equilibrium partitioning method. To meet the Missouri WQS, the WLAs for the facility are set at 5.1 µg/L for Pb and 186.8 µg/L for Zn (see WLA Section as follows).

The TMDL has secondary targets to additionally protect the warm water aquatic life and human health from impairment. Those targets are a threshold effect concentrations for Pb 35.8 mg/kg and Zn 121 mg/kg in sediment.

WLA Comment

Submittal lists individual WLAs for each identified point source [40 CFR § 130.2(h)]. If a WLA is not assigned it must be shown that the discharge does not cause or contribute to WQS excursions, the source is contained in a general permit addressed by the TMDL, or extenuating circumstances exist which prevent assignment of individual WLAs. Any such exceptions must be explained to a satisfactory degree. If a WLA of zero is assigned to any facility it must be stated as such [40 CFR § 130.2(i)]. If this is a phase II TMDL any differences in phase I and phase II WLAs will be documented in this section.

As indicated in the Source Analysis, the only known permitted point source in the watershed is the Doe Run Herculaneum Smelter (MO0000281). This facility has five outfalls, four of which discharge into the Mississippi River and one into Joachim Creek. Outfalls #001 and #003 discharge into the Mississippi River and may have the potential to cause or contribute to the Pb and Zn impairment. 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. Outfalls #004 and #005 discharge storm water runoff from the slag storage area and facility railroad tracks and staging area, respectively. However, these outfalls' Discharge Monitoring Report data are not available.

Based on a LC calculation, the LC is equal to the WLA because the MOS is implicit and the LA is set to 0 lb/day. The following table summarizes the allowable WLAs for dissolved Pb and Zn at several flow conditions.

Percent Flow exceedance	Mississippi River		Joachim Creek	
	Pb (lb/day)	Zn (lb/day)	Pb (lb/day)	Zn (lb/day)
95	2,156	77,800	0.115	4.14
90	2,549	91,965	0.150	5.43
70	3,750	135,304	0.293	10.59
50	4,922	177,587	0.551	19.86
30	6,915	249,468	1.069	38.57
10	11,596	418,387	2.811	101.40
5	14,063	507,392	4.890	176.41

The following table shows the WLA for the Doe Run Herculaneum Smelter (MO0000281). These WLAs were calculated, with consideration of available assimilative capacity of Mississippi River for mixing, and were equal to the WLAs that were determined at the 95 percent flow exceedance. In other words, the combined WLAs for dissolved Pb and Zn from the Doe Run Herculaneum Smelter's Outfall #1 and #3 should not exceed the WLAs calculated at the 95 percent flow exceedance.

Outfall	Design Flow	95 percentile (Maximum) Concentration (µg/L)		Current Loading (lb/day)		WLA (lb/day)	
	cfs	Pb	Zn	Pb	Zn	Pb	Zn
001	1.897	131.31	1553.94	1.34	15.9	2,156	77,800
003	3.610	139.22	39.44	2.71	0.77		

It is very important to note that the allowable WLAs have been calculated for all potential point sources at various flow conditions, which include any unpermitted abandoned mines or tailings piles. Any WLA,

however, does not reflect an authorization to discharge from an unpermitted point source. Discharging Pb and Zn to waters of the Missouri 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 MDNR's permit application and antidegradation processes and will be subject to a thorough evaluation in light of this TMDL.

LA Comment

Includes all nonpoint sources loads, natural background, and potential for future growth. If no nonpoint sources are identified the LA must be given as zero [40 CFR § 130.2(g)]. If this is a phase II TMDL any differences in phase I and phase II LAs will be documented in this section.

The nonpoint sources involve runoff from the areas not associated with the Herculaneum Smelter, including off-site haul and access roads not constructed of waste rock or spent Pb and Zn ore. When compared to the Herculaneum Smelter and historic source areas (i.e., Herculaneum slag pile) of Pb and Zn, nonpoint source loading is expected to be a minor contributor since a majority of the watershed are composed of undisturbed and vegetated areas. This TMDL is specifically derived to target the 5-mile impaired reach. No impairment is noted above and below this reach. Because the Herculaneum smelter has been identified as the principal source of Pb and Zn to the impaired segment and currently there are no known significant nonpoint sources of Pb and Zn from the watershed, and the segment of interest is not listed as impaired in Illinois, LA is set to 0 lb/day.

Margin of Safety

Submittal describes explicit and/or implicit MOS for each pollutant [40 CFR § 130.7(c)(1)]. If the MOS is implicit, the conservative assumptions in the analysis for the MOS are described. If the MOS is explicit, the loadings set aside for the MOS are identified and a rationale for selecting the value for the MOS is provided. If this is a phase II TMDL any differences in MOS will be documented in this section.

The MOS for the Mississippi River TMDL is implicit, because (1) the 25th percentile hardness value of 193 mg $CaCO_3$/L was used in calculating the instream Pb and Zn standards, instead of using the concurrent hardness values and (2) a United State Geological Survey (USGS) gage (ID: 07010000) located above the impaired segment was used to develop the LDCs for the impaired segment. Likewise, a USGS gage (ID: 07018100) was used to estimate the flow for Joachim Creek and its associated metal loads. The MOS for Joachim Creek TMDL is implicit. In the absence of measured water quality data, pore-water Pb and Zn concentrations were calculated from sediment data using an equilibrium partitioning method and was used to evaluate and/or confirm the impairment. Several assumptions regarding the equilibrium partitioning were made. These assumptions are (1) Pb and Zn follow well-defined partitioning behavior between pore water and sediment; and (2) pore water Pb and Zn concentrations were in equilibrium with (or the same as) overlying instream Pb and Zn concentrations. When these metals reside in sediments they exist in equilibrium with pore water. As physical and chemical properties are known, the partitioning behavior of the metals between the sediment and pore water can be predicted.

Seasonal Variation and Critical Conditions

Submittal describes the method for accounting for seasonal variation and critical conditions in the TMDL(s) [40 CFR § 130.7(c)(1)]. Critical conditions are factors such as flow or temperature which may lead to the excursion of WQS. If this is a phase II TMDL any differences in conditions will be documented in this section.

There were insufficient water quality data to determine any seasonal pattern that may be occurring in the Mississippi River watershed. However, the use of LDCs represents the allowable pollutant load under variable flow conditions across all seasons. The results obtained using the LDC method are robust and reliable over all flows and seasons when compared with those obtained under the limited conditions.

Public Participation

Submittal describes required public notice and public comment opportunity, and explains how the public comments were considered in the final TMDL(s) [40 CFR § 130.7(c)(1)(ii)].

The public notice period for the Mississippi River TMDL was from July 30 to September 13, 2010. Groups receiving the public notice announcement included the Missouri Clean Water Commission, 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. In addition, the public notice, the TMDL Information Sheet

and this document were placed on the MDNR's website, making them available to anyone with Internet access. One comment was received on September 13, 2010, and addressed by MDNR. This information will be placed in the Mississippi River docket [file] along with the other documentation.

EPA agrees there had been ample opportunities for the public to participate and submit their comments to MDNR for this TMDL.

Monitoring Plan for TMDL(s) Under Phased Approach

The TMDL identifies a monitoring plan that describes the additional data to be collected to determine if the load reductions required by the TMDL lead to attainment of WQS, and a schedule for considering revisions to the TMDL(s) (where phased approach is used) [40 CFR § 130.7].

Although MDNR has not yet developed a formal monitoring plan, post-TMDL monitoring is often scheduled and carried out by MDNR 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. 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 the post-TMDL conditions. In addition, MDNR will 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 the state on a five to six year rotating schedule.

Reasonable Assurance

Reasonable assurance only applies when less stringent WLAs are assigned based on the assumption of nonpoint source reductions in the LA will be met [40 CFR § 130.2(i)]. This section can also contain statements made by the state concerning the state's authority to control pollutant loads.

EPA believes that point source permitting authority provides reasonable assurances that the TMDL allocations can be achieved.

MDNR has the authority to issue and enforce state operating permits. Inclusion of effluent limits into a state operating permit and requiring that effluent and instream monitoring be reported to MDNR should provide reasonable assurance that instream WQS will be met. 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 Pb and Zn using the WLAs developed for this TMDL. Future inspections of the Doe Run Herculaneum Smelter facility by MDNR 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.

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.

Nonpoint source reductions are currently not necessary to reduce pollutant loading of Pb and Zn to the impaired portion of the Mississippi River. Reductions obtained by implementing the WLA 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.