Recd 9-14-10


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September 13, 2010

Mr. John Hoke
Water Quality Monitoring and Assessment Section
Water Protection Program
Missouri Department of Natural Resources
P.O. Box 176
Jefferson City, MO 65102-0176

Re: Draft TMDL – Mississippi River

Dear Mr. Hoke:

I am writing you on behalf of The Doe Run Resources Corporation, d/b/a The Doe Run Company, offering comments on the draft TMDL for the Mississippi River. Please find enclosed a memorandum from LimnoTech to John Hoke that provides comments on the draft Mississippi River TMDL. I look forward to receiving a response at your earliest convenience.

Sincerely,

NEWMAN, COMLEY & RUTH P.C.

By: Robert J. Brundage

Robert J. Brundage
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RJB:ccl
Enclosure
cc: LimnoTech (w/encl.)
The Doe Run Company (w/encl.)

LimnoTech
Water | Environment | Scientists | Engineers

# MEMORANDUM

DATE: September 13, 2010

FROM: Hans Holmberg
Kathy Hall

TO: John Hoke, Missouri Department of Natural Resources

CC: Robert Brundage, Newman, Comley & Ruth
Rusty Keller, The Doe Run Company
Aaron Miller, The Doe Run Company

SUBJECT: Review of Draft TMDL for the Mississippi River

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In cooperation with Newman, Comley & Ruth and The Doe Run Company we have completed our review of the draft Total Maximum Daily Load (TMDL) for the Mississippi River, as issued by the Missouri Department of Natural Resources (MDNR) on July 30, 2010. This memorandum presents our comments and recommendations for the draft TMDL.

**Comment #1. Listing status and request that TMDL be rescinded**

The Mississippi River was proposed for delisting on Missouri's 2010 303(d) listing by the Missouri Department of Natural Resources ("MDNR"). MDNR proposed the delisting because the Mississippi River currently meets Missouri's water quality standards. MDNR's proposed delisting was approved by the Clean Water Commission on September 8, 2010. Because the Mississippi River currently meets Missouri's water quality standards, a TMDL is not needed, and this TMDL should be rescinded.

In an August 24, 2010, meeting with MDNR and EPA, MDNR stated that a TMDL must be drafted for the Mississippi River because the Mississippi River is included in the list of TMDLs that must be developed based on the settlement agreement and Consent Decree with the American Canoe Association. Under the settlement agreement, MDNR stated that the TMDL must be completed by December 31, 2010. Because of the December 31, 2010, deadline, MDNR stated there is not time to allow Missouri's proposed 303(d) list and Missouri's proposed delisted streams to be approved by EPA, and therefore the draft TMDL must be finalized. Doe Run disagrees that this TMDL must be developed and requests that the TMDL be rescinded. In the past, EPA has issued separate 303(d) list approvals/disapprovals and decisions documents. In the event EPA does not have sufficient time to issue a comprehensive decision of Clean Water Commission's proposed 2010 303(d) list, Doe Run asks EPA to separately approve delisting of the Mississippi before December 31, 2010. Without question, EPA can review and make a decision on the delisting of this water body prior to December 31, 2010.

The Mississippi River was not on Missouri's proposed 1998 303(d) list when the 303(d) list was placed on public notice in August 1998. Instead, the Mississippi River was added to the 303(d) list after comments from EPA stating that all state boundary waters, including both the Mississippi and Missouri Rivers, should be included. The entire 195-mile stretch of the Mississippi River was added to the 303(d) list as being impaired for habitat loss caused by channelization.

In 2002, the Mississippi River was included on the Missouri 303(d) list. The list indicated impairments for chlordane and PCBs (for Water Body Identification ["WBID"] Numbers 1, 3152, and 1707), and for lead

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and zinc (for WBID 1707). The impaired length for the lead and zinc impairments were listed as being approximately five miles.

The Mississippi River was not included on Missouri's proposed 2004/2006 303(d) list, which was approved by the Clean Water Commission in 2007. Instead, MDNR had proposed the Mississippi River for delisting because the available data were inadequate to demonstrate impairment. However, EPA disapproved the delisting, and added the 195.5-mile River back to the 303(d) list. The five-mile segment (WBID 1707) was listed for lead and zinc, and a 124.5-mile segment (WBID 3152) was listed for mercury.

The lead and zinc impairments from WBID 1707 were listed based on one sediment sample with elevated levels of lead and zinc, which was collected near Doe Run Herculaneum's Outfall 001. However, the sample was likely taken within the acute zone of initial dilution and the chronic mixing zone. Other samples were also taken near Herculaneum Outfall 001. These samples included sediment samples, fish tissue, and water quality samples. The results of these data did not support the Mississippi River's inclusion on the 303(d) list for lead and zinc. The data sheets for the 2004/2006 303(d) list are attached as Attachment 1.

In 2006, a TMDL was drafted and approved for the Mississippi River to address the impairments of chlordane and PCB, which were the impairments which placed the Mississippi River on the 303(d) list in 1998.

In 2008, MDNR requested the Mississippi River be delisted for the alleged lead and zinc impairments. The Clean Water Commission granted the delisting. However, EPA again disapproved the delisting, and added the Mississippi River back to Missouri's final 2008 303(d) list. MDNR commented on EPA's addition of the Mississippi River, stating,

> EPA's listing of the [195.5 miles of the Mississippi River] is based on a single sample taken at the area immediately below the outfall of the Herculaneum smelter. The other seventeen (17) sediment samples, some in the vicinity of the smelter outfall, showed only background levels of these two metals. The department agrees that the sample taken at the outfall does exhibit metals contamination, but this one sample is only representative of the immediate area around this outfall.

Additionally, MDNR stated, "the number of events is inadequate to demonstrate impairment. Missouri's listing methodology requires two such occasions in the most recent 3 years of data before we can designate the water as impaired." As discussed above, only one data point from 2001 showed the Mississippi River to be impaired for lead and zinc. In its response to MDNR's comments, EPA refused to delist the Mississippi River.

In the 2008 Missouri 303(d) list, one segment of the Mississippi River (WBID 1707) was again listed for lead and zinc, and another segment (WBID 3152) was listed for mercury.

In 2010, MDNR requested the Mississippi River (WBID 1707) be delisted because water quality standards are now met. Missouri's proposed list was approved by the Clean Water Commission on September 8, 2010, and will be sent to EPA for final approval.

MDNR asserts that, despite proposing delisting of the Mississippi River for the 2010 303(d) list, a TMDL must still be completed pursuant to EPA's settlement agreement with the American Canoe Association.

However, the settlement agreement states, in relevant part, that "EPA is under no obligation to establish TMDLs for any waterbodies that EPA determines do not need TMDLs consistent with Section 303(d) of the CWA ... or are removed from the Missouri Section 303(d) List ... consistent with the provisions of the Clean Water Act and EPA's implementing regulations." Cite, Paragraph 5(b)(4)(B). Because of the Mississippi River's delisting from the 2010 Missouri 303(d) list, a TMDL does not need to be drafted.

EPA has provided conditions that are considered "good cause" for approving delistings. In its Guidance document, 2006 Assessment, Listing and Reporting Requirements Pursuant to Sections 303(d), 305(b) and 314 of the Clean Water Act (hereinafter, "Integrated Report Guidance"), EPA lists a number of "good causes" for removing a water from a 303(d) list. These include, but are not limited to:

- When new information or more sophisticated water quality modeling is available that demonstrates that the applicable WQS(s) is being met;
- When flaws in the original analysis of data and information led to the segment being incorrectly listed;
- The water body and pollutants are addressed in a TMDL approved or established by EPA.
- States may assign waters to Category 4 if available data and/or information indicate that one or more designated uses are not being attained or are threatened, but a TMDL is not needed. States may place these water bodies in one of the following three subcategories:
    - Category 4A: An EPA-approved TMDL has been established to address the water body and pollutant.
    - Category 4B: Alternative pollution controls required by local, state, or federal authority are sufficiently stringent and expected to achieve WQS within a reasonable period of time. One example of such controls is an EPA-approved state National Pollutant Discharge Elimination System (NPDES) Permit in Lieu (PIL) of a TMDL.
    - Category 4C: Impairment not caused by a pollutant, but instead caused by other types of "pollution," as defined by the CWA. Development of TMDL is not required.

Here, MDNR has repeatedly recommended that the Mississippi River should not be listed as impaired due to lead and zinc. The data do not support impairments using MDNR's 303(d) Listing Methodology. The draft TMDL suggests that the existing discharge from Outfall 001 at the Herculaneum Smelting Facility is the only significant source of lead and zinc, and that the levels of lead and zinc being discharged from Outfall 001 are significantly less than the allowable wasteload allocation ("WLA") required to meet water quality standards (less than 0.1% of the draft WLA). Therefore, the TMDL should not be issued based on a flawed listing and recognition that the existing permit is sufficiently stringent to achieve water quality standards.

**Comment 2 – Draft TMDL erroneously includes Joachim Creek**

On Page 3, the draft TMDL states: "Due to 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." However, there are no data presented in the draft TMDL

demonstrating toxicity or impairment of Joachim Creek or the Mississippi River downstream of Joachim Creek.

Page 6 indicates that attempts to analyze sediment samples from Joachim Creek "failed due to a lack of fine sediments downstream of the smelter." Joachim Creek is not included on the 303(d) list. The slag storage area along Joachim Creek is undergoing closure consistent with an Administrative Order on Consent. The closure is intended to prevent any further runoff or leaching from the facility to enter Joachim Creek. Therefore, because there is no data indicating Joachim Creek is impaired, and the slag storage area is already being addressed pursuant to an AOC, Joachim Creek should not be included in the Mississippi River TMDL.

**Comment 3 – Draft TMDL relies on outdated and unreliable data**

The draft TMDL relies on outdated data. Both on Page 7 and in Table 3 of the draft TMDL, there are references to one sediment sample with elevated sediment concentrations. The sediment sample was collected in 2001 in the stormwater outfall to Joachim Creek. This outfall drained to the slag storage area, which is currently undergoing closure. The sample collected in the stormwater outfall is not representative of current or ambient conditions in Joachim Creek or the Mississippi River.

The draft TMDL also relies on data that is not described or presented for verification. For instance, on Page 7, the draft TMDL refers to sediment samples collected in 1995 but provides no other reference to these values or their location. Doe Run is unable to analyze, verify or otherwise look into this value, as not enough information is presented. Additionally, in Section 3.4, MDNR cites the general water quality standards for harming benthic organisms , but presents no direct evidence that the benthic organisms are harmed or impaired due to lead and zinc in the sediment or water column. Because of this lack of information, Doe Run was unable to determine the applicability of the citations.

MDNR also relies on mischaracterized data. On Page 7, the draft TMDL refers to high levels of lead found in fish tissue. However, MDNR provides no data or supporting information on this fish tissue data. The 2004/2006 303(d) list included fish tissue data from 1999 through 2004. A review of that data indicates that only one sample from one carp contained lead levels above the Missouri guideline of 0.3 mg/kg (0.383 mg/kg). Overall, the fish tissue was well below the guidelines, with an upper 60% confidence level of 0.083 mg/kg. At that time the DNR determined that no impairment existed due to fish tissue levels.

**Comment 4 – The draft TMDL erroneously uses pore water concentrations to estimate potential exposure in the water column**

The draft TMDL uses equilibrium partitioning to estimate pore water concentrations in the sediment, then uses the pore water concentrations as an estimate of the *overlying instream concentrations* (page 9). This is a faulty assumption. To assume overlying water column concentrations in the Mississippi River are in equilibrium with pore water concentrations in the sediment is erroneous and unsupported by science.

The draft TMDL states: "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." However, here, the

water body in question is the Mississippi River. Even at critical low-flow conditions, the Mississippi River offers a large amount of dilution of the pore water.

The flaw in MDNR's approach is demonstrated in Figures 5 through 8 of the TMDL report. These figures present a load duration curve, as well as estimates of current loadings of lead and zinc in the Mississippi River and Joachim Creek. The method MDNR used in developing the current loadings is not described in detail in the TMDL, but it appears that estimated pore water concentrations of lead and zinc were multiplied by the flows in the Mississippi River and Joachim Creek on the days the sediment samples were collected. This rests on the assumption that the entire upstream flow in the rivers were at the concentration estimated by equilibrium partitioning with the sediment. This is a mischaracterization of current loadings, and makes it appear as though concentrations of lead and zinc in the water column have exceeded water quality criteria in the rivers while there are no data supporting such exceedances. Instead, the available water column data shows compliance with water quality criteria.

**Comment 5 - Water quality target**

Page 10 indicates that the 25th-percentile hardness for the Mississippi River is 193 mg/l. While this is the 25th-percentile of the paired water quality samples presented in Table 4, additional hardness data are available and should be used. Missouri rules require that hardness be determined by the 25th-percentile of a representative number of samples at the appropriate stream flow conditions. LimnoTech's review of hardness and flow data from the United States Geological Survey (USGS) gaging station #07010000, included below, calculated a 25th-percentile hardness of 215 mg/L.[1] Therefore, the draft TMDL should be updated and 215 mg/L should be used as the hardness value for calculating water quality criteria.

[1] LimnoTech recommends the elimination of the three data points from 1993, as these were collected during record flood levels. The remaining 27 data points from 2004 through 2007 result in a 25th-percentile of 215 mg/L.

**Hardness Data at USGS Station #07010000**

| Date | Hardness, water, milligrams per liter as calcium carbonate |
|---|---|
| 7/18/1993 | 160 |
| 8/10/1993 | 180 |
| 9/2/1993 | 210 |
| 10/26/2004 | 230 |
| 4/12/2005 | 220 |
| 4/22/2005 | 190 |
| 5/10/2005 | 240 |
| 6/10/2005 | 190 |
| 6/21/2005 | 230 |
| 7/12/2005 | 230 |
| 7/20/2005 | 260 |
| 8/9/2005 | 240 |
| 10/4/2005 | 210 |
| 4/10/2006 | 250 |
| 5/1/2006 | 260 |
| 5/2/2006 | 260 |
| 6/2/2006 | 240 |
| 6/5/2006 | 230 |
| 6/12/2006 | 230 |
| 7/24/2006 | 220 |
| 8/22/2006 | 190 |
| 10/17/2006 | 230 |
| 10/23/2006 | 220 |
| 4/11/2007 | 230 |
| 4/23/2007 | 240 |
| 5/29/2007 | 240 |
| 6/25/2007 | 230 |
| 7/16/2007 | 210 |
| 8/21/2007 | 190 |
| 9/7/2007 | 190 |

**Comment 6 – The draft TMDL demonstrates no link between elevated sediment concentrations in one sample and the TMDL's targets for dissolved lead and zinc in the water column**

EPA's *Guidelines for Reviewing TMDLs under Existing Regulations issued in 1992* (EPA, May 20, 2002) states: "the TMDL submittal should explain the linkage between the pollutant of concern and the chosen numeric water quality target." Here, the pollutants of concern in the draft TMDL are lead and zinc. As has been discussed throughout, the alleged impairments are based on one sediment sample in the vicinity of Outfall 001 at the Herculaneum Smelter.

The draft TMDL establishes targets for lead and zinc based on dissolved water quality criteria, and links attainment of these targets to discharges of dissolved lead and zinc from Outfall 001 at the Herculaneum Smelter. However, the draft TMDL does not establish a link between elevated levels of lead and zinc in the sediment and dissolved concentrations of lead and zinc in the water column. While Doe Run does not believe the available data indicate an impairment, even if there is an impairment for lead and zinc in the sediment, it is unclear how achieving dissolved lead and zinc concentrations in the water column reduces lead and zinc in the sediment. Doe Run and LimnoTech ask for clarification on this issue, and, if none can be provided, requests the data be reevaluated to determine there is no impairment to be addressed, or, alternatively, re-formulate the TMDL to address any alleged sediment impairments.

**Comment 7 – The draft TMDL cites technology-based effluent limits as basis for TMDL permit WLAs**

The draft TMDL demonstrates that existing permit (MO-0000337) limits for Outfall 001 at the Herculaneum Smelter are sufficiently stringent to meet the dissolved lead and zinc WLAs presented in Tables 6 and 7, with permit limits that are less than 0.1% of the allowable WLA presented in the TMDL. The existing permit limits for lead and zinc are technology-based limits, not water quality-based limits. Doe Run and MDNR are currently working together to revisit the existing limits as part of the permit renewal process. Therefore, these permit limits should not be referred to in the TMDL. It is sufficient for the TMDL to present the water quality basis for the WLA, and rely on the permit writer to establish permit limits that are protective of water quality and consistent with technology-based requirements.

**Comment 8 – The draft TMDL misrepresents human health as an impaired beneficial use**

Page 13, Section 3.5 of the draft TMDL states that it was necessary to evaluate protectiveness of lead and zinc for human health criteria. The 303(d) listing did not list this beneficial use as impaired, nor are any data presented that indicate human health criteria are not already being protected. Therefore, this section should be deleted from the TMDL.

**Comment 9 –The draft TMDL misrepresents potential for Doe Run discharges to cause or contribute to violations of water quality standards**

Table 10 of the draft TMDL misrepresents the existing Doe Run discharges and the need to reduce zinc discharges by 39% to meet the TMDL. Table 10 used the 95th percentile of the effluent concentrations and the design flow to calculate the current loading. This is an overly conservative representation of the zinc loading from the outfall. In fact, Outfall 001 has not exceeded its daily maximum effluent limit since October 2004, and has only exceeded the monthly average effluent limits three times since 2004. Of the three exceedances: the January 2005 exceedance was 9.8% over the monthly average limitation; the March 2007 exceedance was 36.6% over the monthly average limitation; and the February 2008

exceedance was 1.9% over the monthly average limitation. These effluent data demonstrate that maintaining existing effluent limits is sufficiently protective of water quality standards and the load reductions listed in the TMDL are not necessary.

Appendix A is misleading, as it makes a comparison of Doe Run effluent data to ambient water quality criteria. Identifying effluent concentrations that exceed ambient chronic criteria is not indicative of Doe Run's effect on Mississippi River water quality, given the significant mixing and dilution of the discharge because of the flow in the Mississippi River. Appendix A seems to suggest there are many exceedances of water quality criteria, when in fact there are no data presented to suggest this has occurred. Doe Run asks that the Appendix be revised accordingly.

## Attachment A
## Missouri DNR Data Sheets for 303(d) Listing Determinations for the Mississippi River

### MDNR 2004/2006 303(d) List Data

**Mississippi River- WBID 1707**

Lead in Fish Fillet Tissue, units are mg/kg.

| Org | Site | Site Name | YDATE | SPECIES | NO_SAMPLE | PREP | LNINS | WTLBS | % FAT | Lead |
|---|---|---|---|---|---|---|---|---|---|---|
| MDC | 1707/158.5 | Mississippi R. @ Kimmswick | 1999 | CARP | 25 | F | | 6.5 | 8 | 0.062 |
| MDC | 1707/158.5 | Mississippi R. @ Kimmswick | 2000 | FH CAT | 15 | F | | 1.8 | | 0.01 |
| MDC | 1707/158.5 | Mississippi R. @ Kimmswick | 2001 | FH CAT | 12 | F | | 3.2 | | 0 |
| | | | | | | | | **Average Lead:** | | **0.024** |
| EPA/MDNR | 1707/153.5 | Mississippi R. 2.5 mi.ab. Herculaneum | 2002 | CARP | 5 | F | | 3.6 | | 0.085 |
| EPA/MDNR | 1707/153.5 | Mississippi R. 2.5 mi.ab. Herculaneum | 2002 | W BASS | 5 | F | | 0.6 | | 0.085 |
| EPA/MDNR | 1707/153.5 | Mississippi R. 2.5 mi.ab. Herculaneum | 2003 | CH CAT | 3 | F | | 13.6 | | 0.085 |
| EPA/MDNR | 1707/153.5 | Mississippi R. 2.5 mi.ab. Herculaneum | 2003 | CARP | 5 | F | | 23.5 | | 0.085 |
| EPA/MDNR | 1707/153.5 | Mississippi R. 2.5 mi.ab. Herculaneum | 2004 | W BASS | 5 | F | 11.4 | 0.4 | | 0.085 |
| EPA/MDNR | 1707/153.5 | Mississippi R. 2.5 mi.ab. Herculaneum | 2004 | C CARP | 5 | F | 23.9 | 5.6 | | 0.085 |
| | | | | | | | | **Average Lead:** | | **0.085** |
| MDC | 1707/149 | Mississippi R. @Crystal City | 1999 | STUR | 15 | F | | 1.8 | 6 | 0.036 |
| MDC | 1707/149 | Mississippi R. @Crystal City | 2000 | FH CAT | 17 | F | | 2.8 | 1 | 0.05 |
| MDC | 1707/149 | Mississippi R. @Crystal City | 2001 | FH CAT | 15 | F | | 3.2 | | 0 |
| EPA/MDNR | 1707/149 | Mississippi R. @Crystal City | 2002 | CARP | 5 | F | | 4.2 | | 0.085 |
| EPA/MDNR | 1707/149 | Mississippi R. @Crystal City | 2002 | W BASS | 5 | F | | 0.8 | | 0.085 |
| EPA/MDNR | 1707/149 | Mississippi R. @Crystal City | 2003 | CARP | 5 | F | | 18.7 | | 0.085 |
| EPA/MDNR | 1707/149 | Mississippi R. @Crystal City | 2003 | SAUGER | 3 | F | | 2.5 | | 0.085 |
| EPA/MDNR | 1707/149 | Mississippi R. @Crystal City | 2004 | W BASS | 5 | F | 13.5 | 1 | | 0.085 |
| EPA/MDNR | 1707/149 | Mississippi R. @Crystal City | 2004 | C CARP | 5 | F | 21.9 | 4.1 | | 0.383 |
| MDC | 1707/149 | Mississippi R. @Crystal City | 2004 | SHSTUR | 5 | F | | 2.1 | 7 | 0 |
| MDC | 1707/149 | Mississippi R. @Crystal City | 2004 | SHSTUR | 5 | F | | 1.5 | 7 | 0 |
| MDC | 1707/149 | Mississippi R. @Crystal City | 2004 | SHSTUR | 5 | F | | 1.8 | 4 | 0 |
| | | | | | | | | **Average Lead:** | | **0.075** |
| | | | | | | | | **Std. Deviation:** | | **0.104** |
| | | | | | | | | **60% UCL:** | | **0.083** |
| MDC | 1707/53.0 | Mississippi R. @ Cape Girardeau,MO. | 2000 | FH CAT | 13 | F | | 1.5 | | 0.02 |
| MDC | 1707/53.0 | Mississippi R. @ Cape Girardeau,MO. | 2004 | SHSTUR | 5 | F | | 2.4 | 4 | 0 |
| MDC | 1707/53.0 | Mississippi R. @ Cape Girardeau,MO. | 2004 | SHSTUR | 5 | F | | 2.2 | 7 | 0 |
| MDC | 1707/53.0 | Mississippi R. @ Cape Girardeau,MO. | 2004 | SHSTUR | 5 | F | | 2.4 | 7 | 0 |
| | | | | | | | | **Average Lead:** | | **0.005** |

Recent data for lead in fish tissue in the Mississippi River between the Missouri and the Ohio Rivers is presented here. The guideline level that Missouri bases its assessments on is 0.3 mg/kg. In order for a water to be considered impaired, the 60% upper confidence limit of the data set must be higher than that level, as described in Missouri's 303(d) listing methodology. Out of 12 samples at Crystal City, just below the Herculaneum lead smelter, only one sample exceeded the guideline, and the others showed very low lead levels or were non-detects. Both the average lead level and the 60% UCL at this site were well below 0.3 mg/kg. Therefore, it is recommended that this portion of the Mississippi River be considered not to be impaired due to lead in fish tissue, and that this impairment be removed from Missouri's 2006 303(d) list.

Missouri Department of Natural Resources, Water Protection Program. 573/751-1300

8/7/2006

## MDNR 2004/2006 303(d) List Data (cont.)

### Mississippi R. - WBID 0001, 1707, 3152

Levels of Heavy Metals in Sediments in mg/Kg since 1998

| WBID | SITE NAME | Year | Aluminum | Arsenic | Chromium | Copper | Nickel | Lead | Zinc | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MISSISSIPPI R. MILE 359 (ALEXANDRIA) | 1999 | 19200 | 14 | 27.3 | 9.19 | 17 | 10.9 | 43.7 | |
| 1 | MISSISSIPPI R. MILE 318.9(HANNIBAL) | 1999 | 14400 | 8.44 | 21.1 | 6.76 | 11 | 8.25 | 30.6 | |
| 1707 | MISSISSIPPI R. MILE 165.7(ST.L) | 1999 | 19600 | 13.9 | 30.9 | 11.7 | 17.2 | 7.24 | 39 | |
| 1707 | MISSISSIPPI R. MILE 43.7(CAPE G.) | 1999 | 27100 | 12.9 | 34.8 | 23.5 | 19.2 | 14.1 | 53.9 | |
| 1707 | MISSISSIPPI R. MILE 150.6 bl. Joachim | 2004 | 13600 | 5.33 | 15.4 | 10.28 | 13.3 | 13.3 | 47.6 | 0.25 |
| 1707 | MISSISSIPPI R. MILE 151.4 bl. Joachim | 2004 | 8090 | 4.88 | 11.5 | 5.87 | 10.5 | 9.02 | 43.9 | 0.151 |
| 1707 | MISSISSIPPI R. MILE 153.7 ab. Joachim | 2004 | 19800 | 6.53 | 19.9 | 12.9 | 16.3 | 13.1 | 56.5 | 0.26 |
| 1707 | MISSISSIPPI R. MILE 146.1 bl. Joachim | 2001 | | 5.08 | 23 | 6.98 | 11.7 | 11.8 | 39.4 | 0.373 |
| 1707 | MISSISSIPPI R. MILE 154.2 ab. Joachim | 2004 | 6940 | 4 | 10 | 5.1 | 9.61 | 8.06 | 45.2 | 1.14 |
| 1707 | MISSISSIPPI R. MILE 147.8 bl. Joachim | 2001 | | 5.95 | 24.5 | 8.51 | 14.5 | 11.7 | 49.8 | 0.237 |
| 1707 | MISSISSIPPI R. MILE 152.5 bl. Joachim | 2001 | | 4.36 | 16.3 | 6.5 | 10.3 | 21.3 | 33.6 | 0.293 |
| 1707 | MISSISSIPPI R. MILE 154.2 ab. Joachim | 2001 | | 7.5 | 31.6 | 13.75 | 19.25 | 16.9 | 60.6 | 0.372 |
| 1707 | MISSISSIPPI R. MILE 152 @smelter | 2001 | | 7.56 | 0.02499 | 145 | 35.3 | 1710 | 4920 | 4.02 |
| 3152 | MISSISSIPPI R. MILE 845 (CARUTHERS) | 1999 | 28900 | 16.1 | 36.5 | 14.9 | 22.9 | 17.5 | 77.7 | |
| **Sediment Chemistry PELs*** | | | **60000** | **48** | **120** | **100** | **33** | **82** | **540** | **3.2** |
| **Mean for WBID 1707** | | | **15855** | **7.09** | **19.8114** | **22.735** | **16.1** | **167** | **490** | **0.788** |

Note: Waters are judged to be unimpaired by toxics if there is no more than one exceedence of a toxic criterion in a three year period. There has been only one exceedence on the Mississippi (in the immediate vicinity of the smelter outfall). Thus, this stream is judged to be unimpaired by heavy metals in stream sediments. Lead and zinc are proposed for deletion as pollutants on the 2006 303(d) list for waterbody 1707.

* PEL= Probable Effect Level, the lowest contaminant level at which an adverse effect upon the aquatic biota could be expected.

* No sediment standards appear in state regulations. The criteria here are the Probable Effect Levels (PELs) for heavy metals published in "Calculation and Evaluation of Sediment Effect Concentrations for the Amphipod Hyalella azteca and the Midge Chironomus riparius". Ingersoll et al, J. Great Lakes Res. 22(3):602-623.

Missouri Department of Natural Resources, Water Protection Program. 573/751-1300

8/30/2006

# MDNR 2008 303(d) List Data Sheet

**Missouri Department of Natural Resources**
**Mississippi River - WBID 1707**
**Sediment Chemistry, 1999-2004**
Data is in mg/kg, except HG (ug/kg)

| ORG | SITE | DATE | SITE NAME | AL | AS | BA | CD | CO | CR | CU | FE | HG | MN | NI | PB | ZN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MoDNR | 1707 | 19990616 | MISSISSIPPI R. MILE 165.7(ST.L) | 19600 | 13.9 | 218 | 0.571 | 7.42 | 30.9 | 11.7 | 14300 | 40 | 460 | 17.2 | 7.24 | 39 |
| IEPA | 1707/162.5 | 20010927 | Mississippi R. 1 mi.ab. Meramec R. | | 4.3 | 140 | 0.2499 | | 12 | 10 | 14000 | | 810 | 15 | | 60 |
| MoDNR | 1707/160.9 | 20011205 | Mississippi R. 1 mi.bl. Meramec R. | | 4.34 | | 0.099 | 4.73 | 16.9 | 6.95 | | 19.99 | | 11 | 13.7 | 32.6 |
| MoDNR | 1707/154.2 | 20011205 | Mississippi R. 1.5 mi.ab. Joachim Cr. LDB | | 7.5 | | 0.372 | 8.22 | 31.6 | 13.8 | | 19.99 | | 19.3 | 16.9 | 60.6 |
| MoDNR | 1707/154.2 | 20040729 | Mississippi R. 1.5 mi.ab. Joachim Cr. LDB | 6940 | 4 | 123 | 1.14 | 6.66 | 10 | 5.1 | 10900 | 16 | 409 | 9.61 | 8.06 | 45.2 |
| MoDNR | 1707/153.7 | 20040729 | Mississippi R. 1 mi.ab. Joachim Cr. RDB | 19800 | 6.53 | 170 | 0.26 | 10.7 | 19.9 | 12.9 | 20300 | 21.7 | 793 | 16.3 | 13.1 | 56.5 |
| | | | **Mean** | **15447** | **7** | **163** | **0** | **8** | **20** | **10** | **14875** | **24** | **618** | **15** | **12** | **49** |
| | | | **Probable Effect Level** | | **33** | | **4.98** | | **111** | **149** | | | | **48.6** | **128** | **459** |
| MoDNR | 1707/152.75 | 20011206 | Mississippi R.@smelter outfall, RDB | | 7.56 | | 4.02 | 147 | 0.25 | 145 | | 19.99 | | 35.3 | 1710 | 4920 |
| MoDNR | 1707/152.5 | 20011205 | Mississippi R. 0.2 mi.bl. Joachim Cr., RDB | | 4.36 | | 0.293 | 4.57 | 16.3 | 6.5 | | 19.99 | | 10.3 | 21.3 | 33.6 |
| MoDNR | 1707/151.4 | 20040729 | Mississippi R. 0.5 mi.bl. Joachim Cr. LDB | 8090 | 4.88 | 114 | 0.151 | 7.12 | 11.5 | 5.87 | 12100 | 16.7 | 406 | 10.5 | 9.02 | 43.9 |
| MoDNR | 1707/150.6 | 20040729 | Mississippi R. 1.3 mi.bl. Joachim Cr. RDB | 13600 | 5.33 | 168 | 0.25 | 9.2 | 15.4 | 10.3 | 15450 | 18 | 650 | 13.3 | 13.3 | 47.6 |
| MoDNR | 1707/147.8 | 20011205 | Mississippi R. 4.9 mi.bl. Joachim Cr. | | 5.95 | | 0.237 | 5.48 | 24.5 | 8.51 | | 19.99 | | 14.5 | 11.7 | 49.8 |
| MoDNR | 1707/146.1 | 20011205 | Mississippi R. 6.6 mi.bl. Joachim Cr. | | 5.08 | | 0.373 | 4.89 | 23 | 6.98 | | 19.99 | | 11.7 | 11.8 | 39.4 |
| IEPA | 1707/111 | 20010928 | Mississippi R. ab. Chester, IL | | 7.3 | 210 | 0.55 | | 18 | 18 | 23000 | | 1300 | 24 | | 75 |
| IEPA | 1707/43.7 | 20010926 | Mississippi R. @ Thebes IL | | 6.5 | 180 | 0.2499 | | 15 | 15 | 17000 | | 1000 | 20 | | 61 |
| MoDNR | 1707 | 19990621 | MISSISSIPPI R. MILE 43.7(CAPE G.) | 27100 | 12.9 | 250 | 0.341 | 6.99 | 34.8 | 23.5 | 19100 | 40 | 565 | 19.2 | 14.1 | 53.9 |
| | | | **Mean** | **16263** | **7** | **184** | **0** | **6** | **20** | **12** | **17330** | **22** | **784** | **15** | **14** | **51** |
| | | | **Probable Effect Level** | | **33** | | **4.98** | | **111** | **149** | | | | **48.6** | **128** | **459** |

The U.S. Environmental Protection Agency has not yet established federal guidelines for toxic chemicals in stream or lake sediments. The relationship between the amount of a toxicant in sediment and the strength of the toxicity it exerts is not simple or straightforward. Two publications, *Calculation and Evaluation of Sediment Effect Concentrations for the Amphipod Hyalella azteca and the Midge Chironomus riparus*, C. Ingersoll et al., 1996, and *Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems*, D. MacDonald, et al., 2000, reviewed a large number of research papers on sediment toxicity and suggested numeric guidelines that could be used to judge the potential for toxicity to aquatic life.

The mean levels of metals in the sediments for this segment of the Mississippi are less than the Probable Effect Level, which is the concentration at which some toxic effect on aquatic life is likely, in MacDonald, 2000. Therefore, this segment of the Mississippi River is judged to be unimpaired by metals in the sediment.

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3/31/08 LAT

**Microtox Testing for Sediment Toxicity, 1999-2004**

| | | | | Pore Water (%) | | Solid Phase (mg/L) | |
|---|---|---|---|---|---|---|---|
| ORG | SITE | DATE | SITE NAME | EC20-30min | EC50-30min | EC20-30min | EC50-30min |
| MoDNR | 1707 | 19990616 | MISSISSIPPI R. MILE 165.7(ST.L) | >81.9 | >81.9 | | |
| MoDNR | 1707 | 19990621 | MISSISSIPPI R. MILE 43.7(CAPE G.) | >81.9 | >81.9 | | |
| MoDNR | 1707/150.6 | 20040729 | Mississippi R. 1.3 mi.bl. Joachim Cr. RDB | | | >99000 | >99000 |
| MoDNR | 1707/151.4 | 20040729 | Mississippi R. 0.5 mi.bl. Joachim Cr. LDB | | | >99000 | >99000 |
| MoDNR | 1707/153.7 | 20040729 | Mississippi R. 1 mi.ab. Joachim Cr. RDB | | | >99000 | >99000 |
| MoDNR | 1707/154.2 | 20040729 | Mississippi R. 1.5 mi.ab. Joachim Cr. LDB | | | >99000 | >99000 |

The department screened many of its sediment samples for toxicity using the Microtox testing procedure. The Microtox procedure is not as definitive of a toxicity testing procedure as the common two species (freshwater species, usually a zooplankton and a larval fish species) bioassay procedure. However, Microtox has the advantage of being much easier, quicker and less expensive than traditional bioassay toxicity tests. The Microtox test uses a saltwater alga and measures the amount of light produced and emitted by the alga, refered to as bioluminescence. Reductions in the amount of bioluminescence are interpreted as toxicity. Because this alga does not have the same sensitivity to all toxicants as the most sensitive freshwater fauna in Missouri streams or lake, it isn't a definitive test for the presence or absence of toxicity in Missouri streams or lakes, but it does give some indication for potential toxicity, and relative toxicity where several waters are tested.

The EC50-30min tests for a 50 percent reduction in bioluminescence over a 30-minute period. The EC20-30min tests are more sensitive and test for a 20 percent reduction in bioluminescence over a 30-minute period. In 2003, the department switched from using pore water, the water that fills the spaces between sediment particles, to a solid phase method, which involves soaking the sediment in water to measure the toxicants. Values greater than 99000 or 81.9 percent indicate no toxicity. The lower the value is, the greater the toxicity level.

For the Mississippi River, no samples indicate toxicity.

Missouri Department of Natural Resources, Water Protection Program, 573-751-1300, www.dnr.mo.gov
7/24/08 LAT

## 2010

**Missouri Department of Natural Resources**
**Mississippi River - WBID 1707**
**Sediment Chemistry, 1999-2008**

Data is in mg/kg, except HG (ug/kg)

| ORG | SITE | DATE | SITENAME | AL | AS | BA | CD | CO | CR | CU | FE | HG | MN | NI | PB | ZN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MDNR | 1707 | 19990616 | MISSISSIPPI R. MILE 165.7(ST.L) | 19600 | 13.9 | 218 | 0.571 | 7.42 | 30.9 | 11.7 | 14300 | 39.999 | 460 | 17.2 | 7.24 | 39 |
| MDNR | 1707/188.4 | 20080826 | Mississippi R. @NW end Monsenthein Is. | 17400 | 3.97 | 141 | 0.302 | 9.25 | 21.5 | 13.1 | 20000 | 42.1 | 835 | 17.4 | 12.4 | 65.6 |
| MDNR | 1707/175.5 | 20080826 | Mississippi R. bl. Downtown St.Louis | 14000 | 3.9 | 154 | 0.381 | 8.28 | 18.7 | 11.8 | 17200 | 44.8 | 662 | 15.8 | 13.5 | 69.8 |
| IEPA | 1707/162.5 | 20010927 | Mississippi R. 1 mi.ab. Meramec R. | | 4.3 | 140 | 0.2499 | | 12 | 10 | 14000 | | 810 | 15 | | 60 |
| MDNR | 1707/160.9 | 20011205 | Mississippi R. 1 mi.bl. Meramec R. | | 4.34 | | 0.099 | 4.73 | 16.9 | 6.95 | | 19.99 | | 11 | 13.7 | 32.6 |
| MDNR | 1707/154.2 | 20011205 | Mississippi R. 1.5 mi.ab. Joachim Cr. LDB | | 7.5 | | 0.372 | 8.22 | 31.6 | 13.75 | | 19.99 | | 19.25 | 16.9 | 60.55 |
| MDNR | 1707/154.2 | 20040729 | Mississippi R. 1.5 mi.ab. Joachim Cr. LDB | 6940 | 4 | 123 | 1.14 | 6.66 | 10 | 5.1 | 10900 | 16 | 409 | 9.61 | 8.06 | 45.2 |
| MDNR | 1707/153.7 | 20040729 | Mississippi R. 1 mi.ab. Joachim Cr. RDB | 19800 | 6.53 | 170 | 0.26 | 10.7 | 19.9 | 12.9 | 20300 | 21.7 | 793 | 16.3 | 13.1 | 56.5 |
| | | | **Mean** | **15548** | **6** | **158** | **0** | **8** | **20** | **11** | **16117** | **29** | **662** | **15** | **12** | **54** |
| | | | **Probable Effect Level** | | **33** | | **4.98** | | **111** | **149** | | | | **48.6** | **128** | **459** |
| MDNR | 1707/152.75 | 20011206 | Mississippi R.@smelter outfall, RDB | | 7.56 | | 4.02 | 147 | 0.2499 | 145 | | 19.99 | | 35.3 | 1710 | 4920 |
| MDNR | 1707/152.5 | 20011205 | Mississippi R. 0.2 mi.bl. Joachim Cr., RDB | | 4.36 | | 0.293 | 4.57 | 16.3 | 6.5 | | 19.99 | | 10.3 | 21.3 | 33.6 |
| MDNR | 1707/151.4 | 20040729 | Mississippi R. 0.5 mi.bl. Joachim Cr. LDB | 8090 | 4.68 | 114 | 0.151 | 7.12 | 11.5 | 5.87 | 12100 | 16.7 | 406 | 10.5 | 9.02 | 43.9 |
| MDNR | 1707/151 | 20080827 | Mississippi R. 1 mi.bl. Joachim Cr. | 12100 | 4.02 | 183 | 0.447 | 7.53 | 19.1 | 11.6 | 14600 | 40.8 | 474 | 14.8 | 19.3 | 57.3 |
| MDNR | 1707/150.6 | 20040729 | Mississippi R. 1.3 mi.bl. Joachim Cr. RDB | 13600 | 5.33 | 168 | 0.25 | 9.2 | 15.4 | 10.28 | 15450 | 18 | 650 | 13.3 | 13.25 | 47.6 |
| MDNR | 1707/147.8 | 20011205 | Mississippi R. 4.9 mi.bl. Joachim Cr. | | 5.95 | | 0.237 | 5.48 | 24.5 | 8.51 | | 19.99 | | 14.5 | 11.7 | 49.8 |
| MDNR | 1707/146.1 | 20011205 | Mississippi R. 6.6 mi.bl. Joachim Cr. | | 5.08 | | 0.373 | 4.89 | 23 | 6.98 | | 19.99 | | 11.7 | 11.8 | 39.4 |
| IEPA | 1707/111 | 20010928 | Mississippi R. ab. Chester, IL | | 7.3 | 210 | 0.55 | | 18 | 18 | 23000 | | 1300 | 24 | | 75 |
| IEPA | 1707/43.7 | 20010926 | Mississippi R. @ Thebes IL | | 6.5 | 180 | 0.2499 | | 15 | 15 | 17000 | | 1000 | 20 | | 61 |
| MDNR | 1707 | 19990621 | MISSISSIPPI R. MILE 43.7(CAPE G.) | 27100 | 12.9 | 250 | 0.341 | 6.991 | 34.8 | 23.5 | 19100 | 39.999 | 565 | 19.2 | 14.1 | 53.9 |
| | | | **Mean** | **15223** | **6** | **184** | **0.321** | **7** | **20** | **12** | **16875** | **25** | **733** | **15** | **14** | **51** |
| | | | **Probable Effect Level** | | **33** | | **4.98** | | **111** | **149** | | | | **48.6** | **128** | **459** |

EPA has not yet established federal guidelines for toxic chemicals in stream or lake sediments. The relationship between the amount of a toxicant in sediment and the strength of the toxicity it exerts is not simple or straightforward. Two publications, *Calculation and Evaluation of Sediment Effect Concentrations for the Amphipod Hyalella azteca and the Midge Chironomus riparus*, C. Ingersoll et al., 1996, and *Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems*, D. MacDonald, et al., 2000, reviewed a large number of research papers on sediment toxicity and suggested numeric guidelines that could be used to judge the potential for toxicity to aquatic life.

The mean levels of metals in the sediment for this segment of the Mississippi are less than the Probable Effect Level (the concentration at which some toxic effect on aquatic life is likely) in MacDonald, 2000. Therefore, this segment of the Mississippi River is judged to be unimpaired by metals in the sediment.

MacDonald (2000) found a strong relationship between toxicity and elevated levels of multiple sediment contaminants, even if none of them exceeded their Probable Effects Level values, and proposed the calculation of a sediment quotient. This sediment quotient is calculated by dividing the pollutant concentration in the sample by the Probable Effects Level value for that pollutant. This calculation is made for all sediment pollutants in the sample with PEC values. These calculated values are then summed and normalized by dividing that sum by the number of pollutants.

SQ = [(### mg/kg As/33) + (### mg/kg Cd/4.98) + (### mg/kg CR/111) + (### mg/kg Cu/149) + (### mg/kg Ni/49) + (### mg/kg Pb/128) + (### mg/kg Zn/459)] / 7

SQ = (((6/33)+(0.321/4.98)+(20/111)+(12/149)+(15/48.6)+(14/128)+(51/459))/7) = 0.148

MacDonald found a strong correlation between toxicity and sediment quotients that exceeded 0.5. The sediment quotient for The Mississippi River is 0.148. This is less than the value recommended by MacDonald as a good indicator of toxicity. Therefore, Big Creek is judged to be unimpaired due to the synergistic effects of multiple sediment contaminants.

**Microtox Testing for Sediment Toxicity, 1999-2004**

| | | | | Pore Water (%) | | Solid Phase (mg/L) | |
|---|---|---|---|---|---|---|---|
| ORG | SITE | DATE | SITENAME | EC20-30min | EC50-30min | EC20-30min | EC50-30min |
| MoDNR | 1707 | 19990616 | MISSISSIPPI R. MILE 165.7(ST.L) | >81.9 | >81.9 | | |
| MoDNR | 1707 | 19990621 | MISSISSIPPI R. MILE 43.7(CAPE G.) | >81.9 | >81.9 | | |
| MoDNR | 1707/150.6 | 20040729 | Mississippi R. 1.3 mi.bl. Joachim Cr. RDB | | | >99000 | >99000 |
| MoDNR | 1707/151.4 | 20040729 | Mississippi R. 0.5 mi.bl. Joachim Cr. LDB | | | >99000 | >99000 |
| MoDNR | 1707/153.7 | 20040729 | Mississippi R. 1 mi.ab. Joachim Cr. RDB | | | >99000 | >99000 |
| MoDNR | 1707/154.2 | 20040729 | Mississippi R. 1.5 mi.ab. Joachim Cr. LDB | | | >99000 | >99000 |

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For the Mississippi River, no samples indicate toxicity.

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6/24/2009 RAV