MEMORANDUM | 15 June 2009

TO Suzanne Dudding, U.S. FWS

FROM Ann Shellenbarger Jones and Michael Donlan, IEc

SUBJECT 2008 Grand Lake Sampling Results

As a follow-up to a screening level sediment sampling study conducted in the upper one-third of the lake in 2007, the Oklahoma trustees sampled additional transects in December 2008. The sampling plan included twelve transects with eight sampling points each at a depth of 3-4 inches. The transects covered the entire length of Grand Lake from the confluence of the Neosho and Spring Rivers to the Pensacola Dam. The sampling occurred in December of 2008 and was completed in five days. Samples were collected at all stations except Transect 1-08, Transect 5-08, and Transect 9-01, for a total of 93 samples. The sediment samples were dried and metal concentration was determined by X-ray fluorescence spectrometry (XRF). Voucher samples were sent off for lab analysis as per the EPA 1998 protocol. The 15 voucher samples were also analyzed for simultaneously extracted metal (SEM) and acid volatile sulfide (AVS). By estimating bioavailability, the use of SEM-AVS analysis reduces variability associated with prediction of which sediments will be toxic (EPA 2006).

XRF analyses were conducted in triplicate at the USFWS offices in Manhattan, KS. The average of the three values is used in this analysis. The three primary metals of interest are zinc, lead, and cadmium. Zinc and lead values were above detection limits in all samples, while cadmium was below the detection limit for all samples (detection limits is approximately 40 ppm by XRF).

The voucher samples sent to the laboratory (Trace Element Research Laboratory, at Texas A&M University) confirm the accuracy of the XRF and supported the concentration findings. For zinc, the relative percent difference (RPD) between laboratory and XRF values was 16 percent or less for all samples.[1] The average RPD was 9 percent (with the laboratory results higher than the XRF). For lead, the average RPD was 13 percent (with laboratory results lower than the XRF), with a maximum of 21 percent. Due to the high number of non-detects by XRF for cadmium, a similar analysis was not possible. Laboratory results indicated a very strong relationship between zinc and cadmium concentrations. Due to the high detection limit for cadmium by XRF, we used the laboratory relationship between zinc and cadmium to extrapolate cadmium values from the zinc XRF data.[2] These extrapolated values were then used alongside XRF values for lead and zinc to compare with established thresholds.

Based on comparison of XRF data to a probable effects concentration (PEC)[3], 70 out of the 93 samples exceeded the PEC for zinc (75%). All but two of the sediment samples exceed the threshold effects concentration (TEC) values. For calculated cadmium levels, 5 of 93 samples exceeded the PEC, with 83 of 93 exceeding the TEC (89%). For lead, no samples exceeded the PEC, but 81 exceeded the TEC

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[1] Relative percent difference is calculated as $([Metal]_{lab}-[Metal]_{XRF})/\{([Metal]_{lab}+[Metal]_{XRF})/2\}$.

[2] Based on linear regression from results for the 15 samples analyzed in the laboratory, the relationship between the zinc XRF value and the laboratory cadmium value is expressed as $[Cd] = 0.01[Zn_{XRF}] - 2.474$, with an r^2 value of 0.9038.

[3] McDonald, D.D., Ingersoll, C.G. and Berger, T.A. 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems.

(87%). In all locations, zinc represented the highest level of exceedance for a sample to the TEC or PEC. At least half of the samples in each transect throughout the lake exceeded the PEC for zinc. The calculated values for cadmium did not impact this analysis.

The majority of the zinc values fell between the PEC (459 ppm) and 750 ppm (65 of 93 samples). Five samples were above 750 ppm, with the highest at 1,708 ppm. All five of these samples were from Transect 12 (Stations 4-8), which is located just below the confluence of the Neosho and Spring Rivers. The three lowest zinc values in the study were also for Transect 12 (Stations 1-3); this demonstrates the difference in inputs between the Neosho and Spring Rivers, which do not fully mix for a considerable distance down-lake.

Samples were also compared to the thresholds derived for Tri-State Mining District sediment.[4] These values are predicted to reduce survival of the amphipod *Hyalella azteca* by 10% with exposure to Tri-State Mining District sediments. None of the samples exceeded these thresholds except for two samples for cadmium in Transect 12 (Stations 6 and 8).[5]

The SEM/AVS analysis showed that 6 out of the 15 samples analyzed had a ratio greater than 1 (indicating potential for metals toxicity to sediment-dwelling organisms). All of these samples also exceeded the PEC for zinc. After normalization for organic carbon content[6], one sample from Transect 12 (Station 8) remained above the EPA threshold of 130 $\mu mol/g_{OC}$ (USEPA 2005).[7] This threshold is a general guideline for indicating likelihood of metal toxicity.

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[4] MacDonald D.D., Smorong D.E., Ingersoll C.G., Besser J.M., Brumbaugh W.G., Kemble N.E., May T.E., Ivey C.D., Irving S., O'Hare M. 2009. Development and evaluation of sediment and pore-water toxicity thresholds to support sediment quality assessments in the Tri-state Mining District (TSMD), Missouri, Oklahoma and Kansas. Prepared by USGS, Columbia MO and MacDonald Environmental Sciences Ltd., Nanaimo, BC for the USEPA, Dallas, TX; USEPA, Kansas City, MO; and USFWS, Columbia, MO.

[5] While the evaluation uses extrapolated values for cadmium, laboratory results are also available for Transect 12 Station 8. This value also exceeds the TSMD threshold.

[6] This value is calculated as $(\Sigma SEM\text{-}AVS)/foc$, with the result in micromoles of free metal per gram organic carbon.

[7] USEPA 2005. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metal mixtures (cadmium, copper, lead, nickel, silver, and zinc). EPA-600-R-02-11, Washington DC.

EXHIBIT 1 THRESHOLD EXCEEDANCES FOR GRAND LAKE SEDIMENT

TRANSECT	CADMIUM			LEAD			ZINC			TOTAL NUMBER OF SAMPLES
	% > TEC (0.99 PPM)	% > PEC (4.98 PPM)	% > TSMD (11.1 PPM)	% > TEC (35.8 PPM)	% > PEC (128 PPM)	% > TSMD (150 PPM)	% > TEC (121 PPM)	% > PEC (459 PPM)	% > TSMD (2,083 PPM)	THRESHOLD (VALUE)
1	100%	0%	0%	86%	0%	0%	100%	71%	0%	7
2	100%	0%	0%	100%	0%	0%	100%	75%	0%	8
3	100%	0%	0%	100%	0%	0%	100%	88%	0%	8
4	75%	0%	0%	75%	0%	0%	100%	50%	0%	8
5	100%	0%	0%	86%	0%	0%	100%	86%	0%	7
6	63%	0%	0%	75%	0%	0%	100%	63%	0%	8
7	100%	0%	0%	100%	0%	0%	100%	100%	0%	8
8	75%	0%	0%	75%	0%	0%	100%	75%	0%	8
9	100%	0%	0%	100%	0%	0%	100%	100%	0%	7
10	100%	0%	0%	88%	0%	0%	100%	88%	0%	8
11	100%	0%	0%	100%	0%	0%	100%	50%	0%	8
12	63%	63%	25%	63%	0%	0%	75%	63%	0%	8