

VAN BUREN MUNICIPAL UTILITIES

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“Providing Water, Sewer, and Sanitation Services”
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Attorney
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January 7, 2013

Mr. Kevin Suel
Arkansas Department of Environmental Quality
Water Division Enforcement Branch
5301 Northshore Drive
North Little Rock, AR 72118-5317

Re: NPDES Permit No. AR0021482 & AR0040967, AFIN 17-00062 & 17-00565
Proposed Consent Administrative Order (CAO)

Dear Mr. Suel:

In response to the proposed CAO received on January 4, 2013:

There are three conflicting civil penalty amounts listed. The cover letter states that the penalty amount is Eight Hundred Dollars (\$3,120.00) and page 12 of the CAO states that the amount is Three Thousand One Hundred Fifty Dollars (\$3,150.00). After speaking by telephone on Friday, January 4, 2013 with Mr. Stewart Spencer, ADEQ Attorney, we are assuming that \$3,150.00 is the correct amount; however, we request confirmation.

On page 12 of the CAO; Paragraphs 11, 12, and 13 should refer to the Van Buren Municipal Utilities Commission and the Director of Utilities instead of the City Council, Mayor, and City Clerk/Treasurer.

Main Plant, Permit No. AR0021482

In August of 2011 construction began on a new pump station and force main on South 28th Street in Van Buren at a total estimated final construction cost of \$3,311,575. This facility is one of two stations that deliver wastewater from the Southside sewer collection system to the Main (South) WWTP. The facility is tentatively scheduled to be operating by the end of January 2013. With the completion of the pumping station improvements, it is anticipated that the increased pumping capacity will assist in the reduction of Sanitary Sewer Overflows caused from hydraulic overloading during wet weather conditions. The pump station is designed with variable speed pumps operating

in concert with the previously reconstructed 4th Street Pumping Station to deliver wastewater to the treatment plant at a more uniform and consistent influent flow rate. It is intended that this will also assist the treatment process for the organic and ammonia nitrogen removal issues.

Also, we have been restructuring staff and reevaluating treatment plant control methods and our operations team has been working diligently to achieve consistent nitrification in an attempt to bring the plant into compliance for both organic and ammonia nitrogen.

North Plant, Permit No. 0040967

Please see the attached letter dated September 25, 2012 from the Van Buren Municipal Utilities, and the attached WER Work Plans for Copper and Zinc, which were submitted to the ADEQ by FTN Associates, Ltd.

To date, the Van Buren Municipal Utilities has expended an estimated \$50,000 and invested hundreds of labor hours related to Copper and Zinc limits at this facility. Upon the ADEQ's acceptance of the WER process, we plan to contract with FTN for the development of the WERs for Copper and Zinc at an estimated technical consultant and testing cost of approximately \$60,000.

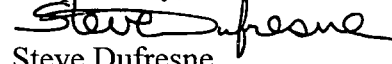
Also, a determination is requested if there is a procedure or methodology that could allow the ADEQ to remove the Copper and Zinc Limits based on the North Plant's discharging into the backwaters of the Arkansas River as has been previously discussed.

I trust that actions taken on our part illustrate the Van Buren Municipal Utilities commitment to continue to address the issues outlined in the CAO.

We respectfully request a 25% reduction in the Three Thousand One Hundred Fifty Dollar (\$3,150.00) civil penalty, which would reduce the penalty to Two Thousand Three Hundred Sixty Two Dollars (\$2,362.00). Furthermore; we request to use 35%, Eight Hundred Twenty Seven Dollars (\$827.00), of the reduced civil penalty on a Supplemental Environmental Project (SEP) to advance environmental interests.

Thank you in advance for these considerations, please contact me if you should have any questions or need further information.

Respectfully,



Steve Dufresne

Director of Utilities

Cc: file
Darel Manus, Operations Superintendent
Larry Weir, P.E., Commission Engineer

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September 25, 2012

Mr. Kevin Suel
Enforcement Analyst
Water Division Enforcement Branch
Arkansas Department of Environmental Quality
5301 Northshore Drive
North Little Rock, AR 72118-5317

Re: NPDES AR0040967, AFIN: 17-00565
Van Buren, Arkansas, North Plant
Copper and Zinc

Dear Mr. Suel:

Per our telephone conversation on September 18, 2012;

1. WER Work Plan

The Van Buren Municipal Utilities has contracted with FTN Associates Ltd. for the preparation and submittal to the ADEQ of a work plan for the development of Water Effect Ratios for Copper and Zinc. (Copy of agreement attached)

2. Summary of Van Buren Municipal Utilities efforts to date to locate sources of influent Copper and Zinc into the North Plant.

Please see attached letter dated September 19, 2012 from C. Larry Weir, P.E., Van Buren Municipal Utilities Commission Engineer.

Based on past correspondence and conversation, the Van Buren Municipal Utilities requests the following consideration;

1. Before undergoing the expense of developing the Water Effect Ratios for Copper and Zinc we wish to know if ADEQ will consider revising the effluent limits for

Page 2

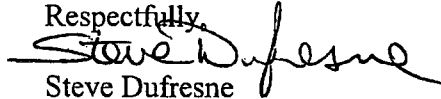
NPDES AR0040967, AFIN: 17-00565, Copper and Zinc

Copper and Zinc at the North Plant should the attached summary and Work Plan be approved, and the WERs show cause for reduction of limits.

2. We wish to know if there is a procedure or methodology that would allow the ADEQ to remove the Copper and Zinc Limits based on the North Plant discharging into the backwaters of the Arkansas River as previously discussed.

Thank you in advance for these considerations, please contact me if you should have any questions or need further information.

Respectfully,



Steve Dufresne
Director of Utilities

Cc: file
Darel Manus, Operations Superintendent
Larry Weir, P.E., Commission Engineer

EXHIBIT A

Scope of Work for Basic Services Proposal to Develop Technical Justification for Water-Effects Ratios for Copper and Zinc

This exhibit is attached to and made part of this Letter Agreement dated September 21, 2012, between FTN Associates, Ltd. (FTN) and Van Buren Municipal Utilities (Client). The 2 tasks of this scope will be to develop water-effects ratios for Cu and Zn. This cost proposal assumes that the supporting data for the Cu WER can be developed using EPA's "streamlined" WER guidance (EPA, 2001)¹ while the supporting data for the Zn WER will be developed using the "interim guidance (EPA, 1994)². The tasks expected to be included in this project are as follows:

TASK 1 PREPARATION AND SUBMITTAL OF WORK PLANS

TASK 1.1 PREPARATION OF COPPER WORK PLAN

FTN will prepare a Draft Work Plan that describes the type, quantity and quality of technical data required to support the Cu WER as well as the required information for the Justification Report. FTN will submit the Draft Work Plan to the Client for review and revise the draft per the Client's review and comment. The data collection and analysis for the Cu WER will follow requirements in EPA's "streamlined" WER guidance (EPA 2001). FTN will submit the draft to ADEQ for review and revise the plan according to comments as necessary to produce Final Work Plan. ADEQ might seek comment and review from Region 6 EPA.

TASK 1.2 PREPARATION OF ZINC WORK PLAN

FTN will prepare a Draft Work Plan that describes the type, quantity and quality of technical data required to support the Zn WER as well as the required information for the Justification Report. FTN will submit the Draft Work Plan to the Client for review and revise the draft per the Client's review and comment. The data collection and analysis for the Zn WER will follow requirements in EPA's original WER guidance (EPA 1994). FTN will submit the draft to ADEQ for review and revise the plan according to comments as necessary to produce Final Work Plan. ADEQ might seek comment and review from Region 6 EPA.

Task 1 lump sum fee: [REDACTED]

¹ EPA. 1994. Interim guidance on determination and use of water-effect ratios for metals. United States Environmental Protection Agency, Office of Water, EPA-823-B-94-001, February, 1994.

² EPA. 2001. Streamlined water-effect ratio procedure for discharges of copper. United States Environmental Protection Agency, Office of Water, EPA-822-R-01-005, March, 2001.



C. Larry Weir, Professional Engineer

Licensed Civil Engineer - Arkansas, Oklahoma, Georgia and Missouri

September 19, 2012

Mr. Steve Dufresne
Director of Utilities
Van Buren Municipal Utilities
2806 Bryan Road
Van Buren, AR 72956

Re: North Plant AR0040967
Recoverable Copper and Zinc

Dear Mr. Dufresne:

This letter is written in response to our discussions about the efforts of the Van Buren Municipal Utilities to identify the sources of the excessive contributions of copper and zinc to the North Plant collection system deemed to be the cause of the plant's failure to meet specified discharge limits.

As you are aware, the permit referenced by number above set forth limits for total recoverable copper of 9.2 μg (monthly average) and 18.5 μg (7-day average). The limits for zinc were similarly set at 85.5 μg and 171.6 μg .

It was recognized that the subject plant is in a collecting drainage basin that is largely domestic contributors but does include some commercial contributors, those being a commercial truck wash, car washes, as well as retail facilities, auto repair, schools, and so forth.

Our initial thoughts were to confirm the accuracy of our testing results. The laboratory had heretofore been reporting metals contributions in mg/l and there was a need to confirm the detection limits. In January of 2008, a series of influent and effluent tests were recommended and performed at the plant

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for this purpose enlisting the independent testing of another contract laboratory, American Interplex.

A series of samples and testing was performed to determine the typical background wastewater concentrations of copper and zinc from collection areas that are only residential and those that included typical commercial sources. Samples were also tested from the commercial truck wash as well as from car washes.

From August of 2009 through June of 2010, the Utility collected samples from various lines carefully moving up the collection system with the intentional object of locating or eliminating sources. During that time samples of influent and effluent were collected at the treatment plant to determine if peaks of discharged metals were reflected in the plant. Generally the removal efficiency at the treatment plant was noted to be 50.4% for copper and 42.9% for zinc.

Our efforts to locate a definitive source were not successful. The pretreatment coordinator had previously surveyed the collection system for potential contributors but then, in July of 2010, visited and interviewed those likely commercial contributors along the lines for potential other sources. Those interviewed and inspected included Wal-Mart, Lowes, mechanic and body shops, tire shops, and so on. The investigation also included an overview check of chemicals being used for cleaning and waxes that may be discharged routinely to the sewer. Although all were cooperative with an explanation of the difficulties, nothing definitive was determined or located.

We have interviewed the City of Fort Smith, Van Buren's water supplier, and determined that the Fort Smith water supply has a normal copper and zinc concentration of 0.31 µg and 4.9 µg respectively. The drinking water has a maintained pH range of 8.5-9 with an observed average of around 8.3.

The North Plant does not receive hauled wastes for treatment nor is the discharge of haulers allowed within the system. The Utility is not aware of instances of illegal or otherwise approved discharges that would explain the contributions of copper and zinc to the system.

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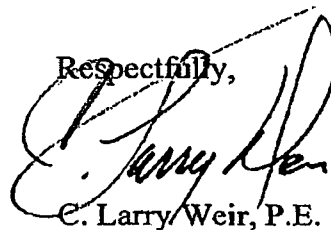
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A point has been made that the discharge of the North Plant to Lee Creek is at an elevation that is below the normal pool elevation of the Arkansas River and consideration was requested for leniency in the discharge limits based on this discharge point being backwater. We are unable to contend that Lee Creek is not intermittent at some times of the year although the Arkansas River does maintain a pool at the location of the discharge.

The Utilities bio-monitoring has not shown there to be a problem with the plant's effluent from that standpoint. In lieu of additional expense, the Utility wishes to verify that the limits are necessary to the extent that they have been set. It is understood that additional specific testing can be performed to establish the limits that would be toxic. The Utility has investigated the determination of the Water Effects Ratio (WER) for both copper and zinc discharges and has discussed this procedure in some depth with FTN Associates. To date FTN has determined from sampling and evaluation that Biotic Ligand Model indicates positive results for justification of higher limits for copper based on the WER. It is possible that a similar circumstance may hold true for Zinc although a model is not readily available for Zinc.

While there is some expense involved with the WER evaluation, it is believed the potential to be far more cost effective to the alternatives of treatment or relocating the discharge from this plant. Another alternative is the continuation of sampling of the collection system in a systematic source of the copper and zinc contributions which may have background domestic points of origin that are not controllable.

Respectfully,

A handwritten signature in black ink, appearing to read "C. Larry Weir", is written over the typed name below.

C. Larry Weir, P.E.

1714 Bunker Hill Drive
Van Buren, Arkansas 72956-2826

telephone - 479.883.1317
c.l.weir@sbcglobal.net



**WORK PLAN TO DEVELOP
A PERMIT TRANSLATOR FOR COPPER
BASED ON A WATER-EFFECTS RATIO**

**VAN BUREN NORTH TREATMENT PLANT
NPDES PERMIT NO. AR0040967**

NOVEMBER 13, 2012

WORK PLAN TO DEVELOP
A PERMIT TRANSLATOR FOR COPPER
BASED ON A WATER-EFFECTS RATIO

VAN BUREN NORTH TREATMENT PLANT
NPDES PERMIT NO. AR0040967

Prepared for

Arkansas Department of Environmental Quality
5301 Northshore Drive
North Little Rock, AR 72118

Submitted by

Van Buren Municipal Utilities Commission
Van Buren North Treatment Plant
2806 Bryan Road
PO Box 1269
Van Buren, AR 72957

Prepared by

FTN Associates, Ltd.
3 Innwood Circle, Suite 220
Little Rock, AR 72211

FTN No. 4000-040

November 13, 2012

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1.0 INTRODUCTION

The purpose of this document is to present a work plan for conducting a water-effects ratio (WER) study for Outfall 001 of the Van Buren North Treatment Plant located in Van Buren, Arkansas (National Pollutant Discharge Elimination System [NPDES] Permit No. AR0040967). The WER study is being proposed as provided in Arkansas Pollution Control and Ecology Commission (APCEC) Regulation No. 2, *Regulation Establishing Water Quality Standards for Surface Waters of the State of Arkansas* (2011). Section 2.308 of Regulation No. 2 allows alternative chemical-specific water quality criteria (WQC) that reflect site-specific conditions. The objective of this study is to develop the WER to support a modification of the permit limit for copper for the facility's Outfall 001.

1.1 Facility Process Description

The facility has a design flow of 2.0 million gallons per day (MGD) and treats municipal waste. Treatment includes bar screens, three individual systems oxidation ditches with the final clarifiers operated in parallel, followed by UV disinfection. At any time all or any combination of the three systems can be operated. An equalization pond is used during wet weather conditions. Water from the equalization pond is pumped through the treatment system.

1.2 Receiving Stream

Outfall 001 discharges into the Arkansas River via Lee Creek in Segment 3H of the Arkansas River Basin. The receiving stream with US Geological Survey (USGS) 8-digit hydrologic unit code (HUC) 11110104 and Reach No. 002 is a water of the state classified for secondary contact recreation; raw water source for public, industrial, and agricultural water supplies; propagation of desirable species of fish and other aquatic life; and other compatible uses. The reaches of Lee Creek and the Arkansas River that receive the discharge are not listed on the 2012 Arkansas 303(d) list of water quality-limited waterbodies.

1.3 NPDES Permit Limits

Permit limits for the existing NPDES permit are provided in Table 1.1. The discharge routinely exceeds NPDES permit limits for copper, which has a 7-day average limit of 18.5 µg/L and a monthly average limit of 9.2 µg/L. The existing copper limits are based on the state's water quality criterion for copper (APCEC 2011), which, in turn, is based on the national criteria.

1.4 Discharge Characteristics

Discharge characteristics (including biomonitoring), as indicated by routine discharge monitoring reports (DMRs), are summarized in Tables 1.2 and 1.3. Under the present permit (Effective March 1, 2008) there have been four whole effluent toxicity (WET) test excursions in routine biomonitoring (Table 1.2). Persistent toxicity was never identified in the required retesting. In addition, Figure 1.1 shows a plot of copper concentrations over time with an indication of the timing of WET excursions. Although samples for copper and WET analyses were not taken at the same time, the plot shows that WET excursions did not occur during periods of relatively high copper concentrations.

This monitoring indicates that:

1. Copper and zinc exceed effluent limitations,
2. The discharge is in general compliance with its permit on other parameters,
3. The discharge has not shown toxicity at the critical dilution (100%) since October 2012, and
4. Previous episodes of toxicity do not correspond to periods of elevated copper concentrations.

Table 1.1. Current NPDES permit discharge limits for Outfall 001.

Effluent Characteristics	Discharge Limitations (mg/L, unless otherwise specified)	
	Monthly Average	7-day Average
Flow	N/A	Report
Carbonaceous Biochemical Oxygen Demand (CBOD ₅)		
May – October	10.0	15.0
November – April	20.0	30.0
Total Suspended Solids (TSS)		
May – October	15.0	22.5
November – April	20.0	30.0
Ammonia Nitrogen		
April	2.2	5.6
May – October	2.0	3.0
November – March	4.0	6.0
Dissolved Oxygen		
May – October	5.0 (Monthly Average Minimum)	
November – April	6.0 (Monthly Average Minimum)	
Fecal Coliform Bacteria (FCB)		
April – September	200 colony-forming units (CFU)/100mL	400 CFU/100mL
October – March	100 CFU/100mL	1,000 CFU/100mL
Copper, Total Recoverable	9.2 µg/L	18.5 µg/L
Zinc, Total Recoverable	85.5 µg/L	171.6 µg/L
pH	Minimum: 6.0 su	Maximum: 9.0 su
<i>Pimephales promelas</i> (Chronic)	7-day Average	
Pass/Fail Lethality (7-day NOEC)	Report (Pass/Fail)	
Pass/Fail Growth (7-day NOEC)	Report (Pass/Fail)	
Survival (7-day NOEC)	Report %	
Coefficient of Variation	Report %	
Reproduction (7-day NOEC)	Report %	
<i>Ceriodaphnia dubia</i> (Chronic)	7-day Average	
Pass/Fail Lethality (7-day NOEC)	Report (Pass/Fail)	
Pass/Fail Growth (7-day NOEC)	Report (Pass/Fail)	
Survival (7-day NOEC)	Report %	
Coefficient of Variation	Report %	
Reproduction (7-day NOEC)	Report %	

Table 1.2. Summary of NOEC (% effluent) from the most recent 3 years of routine biomonitoring at the Van Buren North Treatment Plant Outfall 001.

Sampling Dates	<i>P. promelas</i>		<i>C. dubia</i>	
	Survival	Growth	Survival	Reproduction
04/15/12 – 04/19/12	100	100	100	100
01/15/12-01/19/12	100	100	100	100
11/13/11-11/17/11	100	100	100	100
07/10/11-07/14/11	100	100	100	100
04/03/11-04/07/11	100	100	100	100
03/06/11-03/10/11	No Test	100	100	100
01/23/11-01/27/11	100	100	Control Failure	Control Failure
12/05/10-12/09/10	No Test	100	100	100
11/14/10-11/18/10	100	100	100	100
10/24/10-10/28/10	100	100	100	< 100
07/18/10-07/22/10	100	100	100	100
04/11/10-04/15/10	100	100	100	100
01/10/10-01/14/10	100	100	100	100
11/29/09-12/03/09	100	100	< 100	< 100
11/08/09-11/12/09	100	100	100	100
10/25/09-10/29/09	100	100	100	100
09/13/09-09/17/09	< 100	< 100	100	< 100
08/30/09-09/03/09	No Test	100	100	100
07/26/09-07/30/09	No Test	100	100	100
06/23/09-06/28/09	No Test	100	100	100
06/07/09-06/11/09	100	100	100	< 100
02/22/09-02/26/09	100	100	100	100

Table 1.3. Summary of DMR monitoring at Outfall 001, October 2009 through September 2012.

Summary Statistic	Avg Flow (mgd)	Max Flow (mgd)	CBOD (mg/L)	TSS (mg/L)	FCB (CFU)	pH (min)	pH (max)	DO (mg/L)	NH ₃ -N (mg/L)	Cu (µg/L)	Zn (µg/L)	
Percentile	25	0.79	1.12	3.5	1.8	4.8	6.1	6.6	7.6	0.11	6.3	48.4
	50	1.02	2.01	4.0	2.4	11	6.2	6.7	8.2	0.17	8.0	69.0
	75	1.36	2.70	4.5	3.0	26	6.2	6.8	9.2	0.24	9.1	84.8
	95	1.91	3.89	7.3	5.2	67	6.3	7.0	9.9	0.60	14	164
Minimum	0.56	0.66	3.0	1.0	1.0	6.1	6.2	6.9	0.05	4.7	40.0	
Average	1.12	2.06	4.3	2.6	20	6.2	6.7	8.4	0.23	8.5	79.6	
Maximum	2.15	4.94	7.5	5.8	102	6.4	7.1	10.2	0.98	18	249	

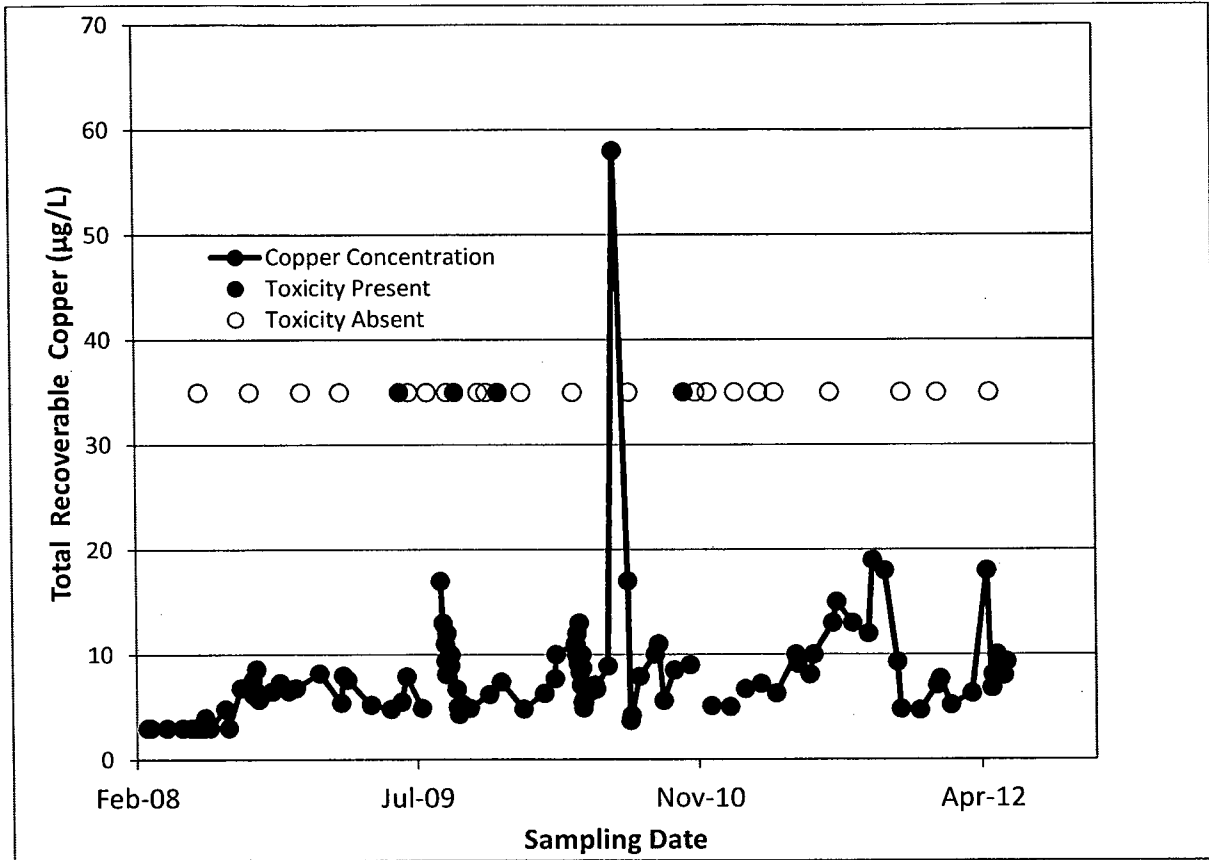


Figure 1.1. Plot of copper concentrations and occurrences of WET excursions.

A summary of copper concentrations and exceedance factors (measured metal concentration ÷ permit limit) for routine effluent monitoring conducted October 2009 through April 2012 data is presented in Table 1.4. The 95th percentile values for the exceedance factors corresponding to the monthly average is 1.6. This result indicates that the existing permit limit for copper need to be increased by a factor of approximately 1.6 to result in permit compliance.

Table 1.4. A summary of copper concentrations and exceedance factors (measured metal concentration ÷ permit limit) for routine effluent monitoring conducted October 2009 through April 2012.

Summary Statistic	Monthly Average	Exceedance Factor
Percentile	25	14.4
	50	9.1
	75	8.0
	95	6.3
Minimum	4.7	0.5
Average	8.5	0.9
Maximum	18.0	2.0

1.4.1 Preliminary WER Evaluation

A preliminary evaluation of the expected WER was made using the biotic ligand model (BLM). The BLM (Di Toro et al. 2001) forms the basis for the US Environmental Protection Agency's (EPA's) ambient water quality criterion for copper (EPA 2007). It predicts copper toxicity to *Ceriodaphnia dubia* and other standard aquatic test species based on measured concentrations of selected cations (e.g., calcium and magnesium), anions (e.g., chloride and sulfate), alkalinity, pH, and dissolved organic carbon. Measured values of these parameters were obtained from a sample collected on July 1, 2012. The model calculation indicated an expected WER of 5.5 (Table 1.5). This result suggests that the permit limit could be adjusted upward by a factor of 5.5, based on the predicted bioavailability of copper in the effluent.

A WER of 5.5 would provide a substantial safety factor if the permit limit were raised by a factor of 1.6 to achieve permit compliance.

Table 1.5. Summary of BLM model results.

Sample	Hardness (mg/L as CaCO ₃)	BLM-Predicted LC50		Adjusted LC50* (µg/L)	Predicted WER (total copper)
		mol/L	µg/L		
Outfall 001	83.5			68.69	5.5
Species Mean Acute Value (SMAV) EC50 (µg/L) from EPA (2001), Appendix B					
Species	Hardness = 50 mg/L		Hardness = 100 mg/L		
	Total Copper (µg/L)	Dissolved Copper (µg/L)	Total Copper (µg/L)	Dissolved Copper (µg/L)	
<i>C. dubia</i>	12.49	11.51	24.00	22.11	

*Hardness of 50 mg/L

1.5 Proposed Approach

Technical guidance for conducting a WER study is provided in EPA's Interim Procedure (EPA 1994) and the Streamlined Procedure (EPA 2001). The Interim Procedure applies to all situations for most metals, whereas the Streamlined Procedure applies only to situations where copper concentrations are elevated primarily by continuous point sources and where copper in the receiving stream is expected to attain its maximum concentrations under low-flow conditions. The Streamlined Procedure is not intended for situations where wet weather or nonpoint sources are the dominant copper sources (EPA 2001). Since Lee Creek is not on the 303(d) list of impaired waters it can be presumed that Lee Creek is meeting water quality standards for copper and that Outfall 001 would represent the major source of copper in the reach of Lee Creek in question. Accordingly, the Streamlined Procedure provides an appropriate approach for WER development for Outfall 001.

2.0 SAMPLING AND TESTING PROTOCOL

The following sampling and testing protocol is based on Appendix A of the Streamlined Procedure (EPA 2001). All toxicity test procedures and analytical testing will be conducted by American Interplex Corporation Laboratories¹ (AIC), which is an Arkansas Department of Environmental Quality (ADEQ)-certified laboratory.

Per the Streamlined Procedure, definitive WER testing as described below will be conducted on two occasions, using samples collected at least 30 days apart.

2.1 Test Organisms

The Streamlined Procedure requires the use of either *C. dubia* or *Daphnia magna* for WER tests. The test organism chosen for this project is *C. dubia*, which is also used in the plant's routine quarterly biomonitoring. Test organisms will be acclimated through special culture conditions (e.g., modified hardness) if warranted. However, special organism acclimation to site water hardness is not anticipated as part of this project. Toxicity tests will be conducted using *C. dubia* cultured in laboratory water with a hardness of 100 mg/L or other level as appropriate. Test organisms will be less than 24 hours of age and within 8 hours of the same age at the beginning of the test. Test organisms will be fed algae before they are transferred to the test chambers to begin the test. However, no food will be placed in the test containers and special care will be taken to prevent the transfer of food to the test containers along with the test organisms when the test is loaded.

2.2 Sample Collection

For WER testing, the Streamlined Procedure stipulates the use of a simulated downstream sample prepared by collecting and mixing samples of effluent and upstream water at the design low-flow dilution. The simulated downstream sample is then used for all toxicity testing and associated chemical analyses. The critical dilution for Outfall 001 is 100%.

¹ 8600 Kanis Road, Little Rock, AR 72011

Accordingly, all testing using the site water (effluent) will be performed using undiluted (100%) effluent.

A 24-hour flow-weighted composite effluent sample will be collected using an automated sampler. Sampler bottles will be washed according to AIC Quality Assurance (QA) Plan specifications (detergent-washed, rinsed in acid+deionized water). Samples to be used for toxicity testing will be maintained unpreserved at 1°C to 4°C during collection shipment and storage. The flow-weighted composite sample will be prepared in the laboratory using flow data provided by plant personnel. Sub-samples of the composite will be collected for analysis of chemical parameters using appropriate sample container cleaning and sample preservation. Samples will be stored at in the dark at 1°C to 4°C with no headspace in the container. The effluent sample will be collected at a time when plant operating conditions are average or better, and when both the discharge and receiving stream are relatively unaffected by short-term perturbations due to rainfall. The receiving stream flows and weather conditions will be documented based on data for two weeks preceding the sampling event from USGS stream monitoring station USGS 07250085 (Lee Creek at Lee Creek Reservoir approximately 1.2 miles upstream of Outfall 001) and the Southern Regional Climate Center Station No. 032574 (Ft. Smith, Arkansas; approximately 9.8 miles SSW of Outfall 001.) Normal operating conditions will be documented based on measurements of CBOD₅, ammonia, total suspended solids (TSS) and flows taken during the time of effluent sampling and compared with values typical for the plant.

Sample delivery to the testing laboratory will include appropriate completed chain-of-custody documentation.

2.3 Laboratory Testing Water

Water used in the laboratory water toxicity tests will be prepared per EPA guidance (EPA 1991). The concentration of total organic carbon (TOC) and TSS in the laboratory water will be less than 0.5 mg/L and less than 4 mg/L, respectively. The concentration of salts used to prepare the laboratory water will be adjusted to provide a hardness of 200 mg/L. This approach will result in laboratory water with (1) levels of alkalinity and pH that are appropriate for the

level of hardness, (2) a measured hardness concentration between 40 and 220 mg/L, and (3) a level of hardness similar to the site water per requirements of EPA (2001).

2.4 Toxicity Tests

2.4.1 Range-Finding Tests

Range-finding tests will be conducted prior to the conduct of definitive toxicity tests used to calculate the WER. The purpose of the range-finding test is to determine the appropriate range of copper concentrations for the definitive tests and to indicate whether or not the definitive tests can be conducted as static renewal or static non-renewal tests. The range-finding tests can also provide a preliminary estimate of the WER. Range-finding tests will be conducted on site water and laboratory water spiked with inorganic copper salts.

The copper stock solution used to spike the site water and laboratory samples will be prepared from deionized water and reagent-grade copper chloride 2-hydrate [$\text{CuCl}_2(2\text{H}_2\text{O})$], copper nitrate 2.5-hydrate [$\text{Cu}(\text{NO}_3)_2(2.5\text{H}_2\text{O})$], or copper sulfate 5-hydrate [$\text{CuSO}_4(5\text{H}_2\text{O})$]. The stock solution will be sufficiently concentrated to prevent significant dilution of the site water or laboratory water with the deionized water matrix. The stock solution will be sufficiently acidified with reagent-grade acid to prevent copper precipitation during storage, while not containing excess acid that will affect the pH of the test solutions.

Tests will be 48-hour static non-renewal tests, with ten organisms per concentration and up to eight copper exposure concentrations using a dilution factor of 0.3. Because the purpose of the range-finding test is to determine the appropriate upper and lower range of copper concentrations for the definitive test, copper concentrations will not be measured at each exposure concentration. However, initial and final copper concentrations will be measured at selected concentrations to evaluate the change in copper concentration occurring in the test beakers during the test. This information will be used to determine the need for static renewals at 24 hours in the definitive tests. Definitive tests will be conducted as static renewal tests if there is greater than a 50% decrease in dissolved copper concentrations between the initial and final values in the range-finding test, or if an unacceptable decrease in dissolved oxygen occurs in the test beakers.

2.4.2 Definitive Tests

Definitive toxicity tests to be used for the calculation of the WER will be designed based on the results of the range-finding tests. For purposes of preparing this protocol, it is assumed that static non-renewal tests will be required. The procedure for the static renewal test will be essentially identical, except for the intervening renewal step. A dilution factor of at least 0.6 will be used to establish the copper concentrations in successive test exposures.

Definitive tests will be conducted using a freshly collected effluent sample. Testing will begin within 96 hours of sample collection. Exposure solutions will be prepared by preparing a large volume of the highest test concentration of site water (effluent/receiving stream mixture) and laboratory water. Serial dilutions of the spiked site water and laboratory water will be prepared using unspiked portions of the site water and laboratory water, respectively, as diluent. The same copper stock solution (prepared as above) will be used to spike both site water and laboratory water samples. The mixed solutions will then be allowed to equilibrate at test temperature for 1 to 4 hours.

After the equilibration period, appropriate volumes (25 mL) of exposure solution will be dispensed into the test chambers. Aliquots of these initial test solutions will be retained for copper analysis as described in following sections. Test organisms will be assigned randomly to the test chambers. Five test chambers, each containing five organisms, will be used for both the site water and laboratory water tests. Four of the chambers will serve as the actual experimental chambers that will provide the counts of surviving organisms. The fifth chamber of each test concentration will be used as a "chemistry control." Routine test measurements such as temperature, dissolved oxygen, and pH will be taken from the chemistry controls to reduce the possibility of cross contamination of test solutions due to the use of instrument probes during routine test maintenance. Test organisms for both the site water and the laboratory tests will be added at the same time (within 0.5 hour). The two tests (site water and laboratory water) will then be conducted so that there are no differences other than the composition of the dilution water and the copper concentrations.

Tests will be maintained and test organism effects/symptoms will be observed and recorded as specified in EPA (1991).

3.0 CHEMICAL AND OTHER MEASUREMENTS

Effluent, receiving stream, and effluent/receiving stream mixture samples collected for each series of tests (including range-finding tests and definitive tests) will be analyzed for the parameters listed in Tables 1.1 and 3.1. This parameter list includes routine NPDES permit parameters that are analyzed to document plant operating conditions and to perform BLM calculations (Di Toro et al. 2001).

Table 3.1. Analytical parameters for water samples to be collected for WER testing.

Parameter	Analytical Method	Reporting Limit (mg/L)
Carbonaceous Biochemical Oxygen Demand	EPA 405.1	1
Total Copper *	EPA 200.8	0.006
Dissolved Copper *	EPA 200.8	0.006
Total Organic Carbon *	EPA 415.1	1.0
Dissolved Organic Carbon *	EPA 415.1	1.0
Total Ammonia	EPA 350	0.5
Total Calcium	EPA 200.8	0.1
Total Magnesium	EPA 200.8	0.03
Total Sodium	EPA 200.8	1.0
Total Potassium	EPA 200.8	1.0
Sulfate	EPA 300.0	0.2
Chloride	EPA 300.0	0.2
pH*	Electrode	NA
Total Alkalinity*	EPA 310.1	1.0
Hardness*	EPA 130.0	1.0
Total Dissolve Solids	EPA 160.1	4.0
Total Suspended Solids *	EPA 160.2	4.0

*Indicates parameters also to be measured in laboratory water.

Samples for the analysis of copper will be collected from each concentration at the beginning and end of each 24-hour period. The sample for the end of a 24-hour period (and/or the end of the test, as appropriate) for a particular test concentration will be collected by combining all four replicates into a single composite. A portion of the composite will then be filtered through a 0.45- μ membrane filter. The preserved copper samples will be analyzed as a

single batch at the end of the end of the test. Analyses will be conducted only on those concentrations necessary for LC50 calculations.

4.0 DATA QUALITY OBJECTIVES

Toxicity testing and analytical procedures and results will undergo Quality Assurance/Quality Control (QA/QC) review as specified in AIC's written QA/QC procedures. Toxicity test acceptance criteria are summarized in Table 4.1. Acceptance criteria for chemical analyses are provided in Table 4.2. Toxicity tests that do not meet acceptance criteria will not be considered valid for the study purposes. Chemical analyses that do not meet acceptance criteria will be repeated, if possible. The need to invalidate testing based on failure to meet acceptance criteria for chemical analyses will be determined, with agency consultation, based on the type and severity of the failure. Toxicity and analytical tests may also be invalidated for additional reasons identified during the routine QA/QC review performed by AIC.

Table 4.1. Acceptance criteria for toxicity tests.

Test Parameter	Acceptance Criterion
Temperature	25°C ± 1°C ^(a)
Dissolved oxygen	> 6 mg/L in all test concentrations ^(b)
pH	6.5 – 8.5 su ^(c)
Performance control survival	≥ 90% ^(a,c)
Unspiked effluent control	≥ 90% ^(a,c)
Percent decrease in dissolved metal concentration between initial and final measurements	< 50% ^(c)
Percent of adversely affected organisms in laboratory water test	> 50% in at least one test concentration ^(c)
Percent of adversely affected organisms in effluent test	< 50% in at least one test concentration ^(c)
Dose response	Inverted dose response does not affect more than two concentrations having between 20% and 80% mortality ^(c)

Notes:

- a. Based on EPA (1991).
- b. Based on typical levels observed during routine biomonitoring.
- c. Based on EPA (1994).

Table 4.2. Acceptance criteria for chemical analyses.

Analytical Parameter	Quality Control Parameter		
	Duplicate RPD	LCS % Recovery	Laboratory Blank (mg/L)
Biochemical Oxygen Demand	± 20%	85 – 115%	< 1.0
Total Copper	± 20%	85 – 115%	<0.006
Dissolved Copper	± 20%	NA	< 0.006
Total Organic Carbon	± 20%	NA	<1.0
Dissolved Organic Carbon	± 20%	NA	<1.0
Total Ammonia	± 20%	85 – 115%	<0.5
Total Calcium	± 20%	85 – 115%	<0.1
Total Magnesium	± 20%	85 – 115%	<0.03
Total Sodium	± 20%	85 – 115%	<1.0
Total Potassium	± 20%	85 – 115%	<1.0
Sulfate	± 20%	90 – 110%	<0.2
Chloride	± 20%	90 – 110%	<0.2
Total Alkalinity	± 20%	N/A	<1.0
Hardness	± 20%	85 – 115%	<1.0
TSS	± 20%	NA	<4.0
Total Dissolved Solids	± 20%	85 – 115%	<4.0

6.0 REPORTING RESULTS

A report of the results will be prepared containing, at a minimum, the information required by Appendix A, Section H of EPA's Streamlined Procedure (2001).

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**WORK PLAN TO DEVELOP
A PERMIT TRANSLATOR FOR ZINC BASED ON
A WATER-EFFECTS RATIO**

**VAN BUREN, OUTFALL 001
NPDES PERMIT NO. AR0040967**

**DRAFT
DECEMBER 3, 2012**

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1.0 INTRODUCTION

The purpose of this document is to present a work plan for conducting a water-effects ratio (WER) study for Outfall 001 of the Van Buren North Treatment Plant located in Van Buren, Arkansas (National Pollutant Discharge Elimination System [NPDES] Permit No. AR0040967). The objective of this study is to develop the WER to support a modification of the permit limit for zinc for the facility's Outfall 001.

1.1 Facility Process Description

The facility has a design flow of 2.0 million gallons per day (MGD) and treats municipal waste. Treatment includes bar screens, three individual systems oxidation ditches with the final clarifiers operated in parallel, followed by UV disinfection. At any time all or any combination of the three systems can be operated. An equalization pond is used during wet weather conditions. Water from the equalization pond is pumped through the treatment system.

1.2 NPDES Permit Limits

Permit limits for the existing NPDES permit are provided in Table 1.1. The discharge exceeds monthly average permit limits (85.5 $\mu\text{g/L}$) for Zinc in approximately 12% of samples. The existing zinc limits are based on the state's water quality criterion for zinc (APCEC 2011), which, in turn, is based on the national criteria.

1.3 Discharge Characteristics

Discharge characteristics (including biomonitoring), as indicated by routine discharge monitoring reports (DMRs), are summarized in Tables 1.2 and 1.3. Under the present permit (effective March 1, 2008) there have been four whole effluent toxicity (WET) test excursions in routine biomonitoring (Table 1.2). Persistent toxicity was never identified in the required retesting. In addition, Figure 1.1 shows a plot of zinc concentrations over time with an indication of the timing of WET excursions. Although samples for zinc and WET analyses were not taken

at the same time, the plot shows that WET excursions did not occur during periods of relatively high zinc concentrations.

This monitoring indicates that:

1. Copper and zinc exceed effluent limitations,
2. The discharge is in general compliance with its permit on other parameters,
3. The discharge has not shown toxicity at the critical dilution (100%) since October 2010, and
4. Previous episodes of toxicity do not correspond to periods of elevated zinc concentrations.

Table 1.1. Current NPDES permit discharge limits for Outfall 001.

Effluent Characteristics	Discharge Limitations (mg/L, unless otherwise specified)	
	Monthly Average	7-day Average
Flow	N/A	Report
Carbonaceous Biochemical Oxygen Demand (CBOD ₅)		
May – October	10.0	15.0
November – April	20.0	30.0
Total Suspended Solids (TSS)		
May – October	15.0	22.5
November – April	20.0	30.0
Ammonia Nitrogen		
April	2.2	5.6
May – October	2.0	3.0
November – March	4.0	6.0
Dissolved Oxygen		
May – October	5.0 (Monthly Average Minimum)	
November – April	6.0 (Monthly Average Minimum)	
Fecal Coliform Bacteria (FCB)		
April – September	200 colony-forming units (CFU)/100mL	400 CFU/100mL
October – March	100 CFU/100mL	1,000 CFU/100mL
Copper, Total Recoverable	9.2 µg/L	18.5 µg/L
Zinc, Total Recoverable	85.5 µg/L	171.6 µg/L
pH	Minimum: 6.0 su	Maximum: 9.0 su
<i>Pimephales promelas</i> (Chronic)	7-day Average	
Pass/Fail Lethality (7-day NOEC)	Report (Pass/Fail)	
Pass/Fail Growth (7-day NOEC)	Report (Pass/Fail)	
Survival (7-day NOEC)	Report %	
Coefficient of Variation	Report %	
Reproduction (7-day NOEC)	Report %	
<i>Ceriodaphnia dubia</i> (Chronic)	7-day Average	
Pass/Fail Lethality (7-day NOEC)	Report (Pass/Fail)	
Pass/Fail Growth (7-day NOEC)	Report (Pass/Fail)	
Survival (7-day NOEC)	Report %	
Coefficient of Variation	Report %	
Reproduction (7-day NOEC)	Report %	

Table 1.2. Summary of NOEC (% effluent) from the most recent 3 years of routine biomonitoring at the Van Buren North Treatment Plant Outfall 001.

Sampling Dates	<i>P. promelas</i>		<i>C. dubia</i>	
	Survival	Growth	Survival	Reproduction
04/15/12 – 04/19/12	100	100	100	100
01/15/12-01/19/12	100	100	100	100
11/13/11-11/17/11	100	100	100	100
07/10/11-07/14/11	100	100	100	100
04/03/11-04/07/11	100	100	100	100
03/06/11-03/10/11	No Test	100	100	100
01/23/11-01/27/11	100	100	Control Failure	Control Failure
12/05/10-12/09/10	No Test	100	100	100
11/14/10-11/18/10	100	100	100	100
10/24/10-10/28/10	100	100	100	< 100
07/18/10-07/22/10	100	100	100	100
04/11/10-04/15/10	100	100	100	100
01/10/10-01/14/10	100	100	100	100
11/29/09-12/03/09	100	100	< 100	< 100
11/08/09-11/12/09	100	100	100	100
10/25/09-10/29/09	100	100	100	100
09/13/09-09/17/09	< 100	< 100	100	< 100
08/30/09-09/03/09	No Test	100	100	100
07/26/09-07/30/09	No Test	100	100	100
06/23/09-06/28/09	No Test	100	100	100
06/07/09-06/11/09	100	100	100	< 100
02/22/09-02/26/09	100	100	100	100

Table 1.3. Summary of DMR monitoring at Outfall 001, October 2009 through September 2012.

Summary Statistic	Avg Flow (mgd)	Max Flow (mgd)	CBOD (mg/L)	TSS (mg/L)	FCB (CFU)	pH (min)	pH (max)	DO (mg/L)	NH ₃ -N (mg/L)	Cu (µg/L)	Zn (µg/L)	
Percentile	25	0.79	1.12	3.5	1.8	4.8	6.1	6.6	7.6	0.11	6.3	48.4
	50	1.02	2.01	4.0	2.4	11	6.2	6.7	8.2	0.17	8.0	69.0
	75	1.36	2.70	4.5	3.0	26	6.2	6.8	9.2	0.24	9.1	84.8
	95	1.91	3.89	7.3	5.2	67	6.3	7.0	9.9	0.60	14	164
Minimum	0.56	0.66	3.0	1.0	1.0	6.1	6.2	6.9	0.05	4.7	40.0	
Average	1.12	2.06	4.3	2.6	20	6.2	6.7	8.4	0.23	8.5	79.6	
Maximum	2.15	4.94	7.5	5.8	102	6.4	7.1	10.2	0.98	18	249	

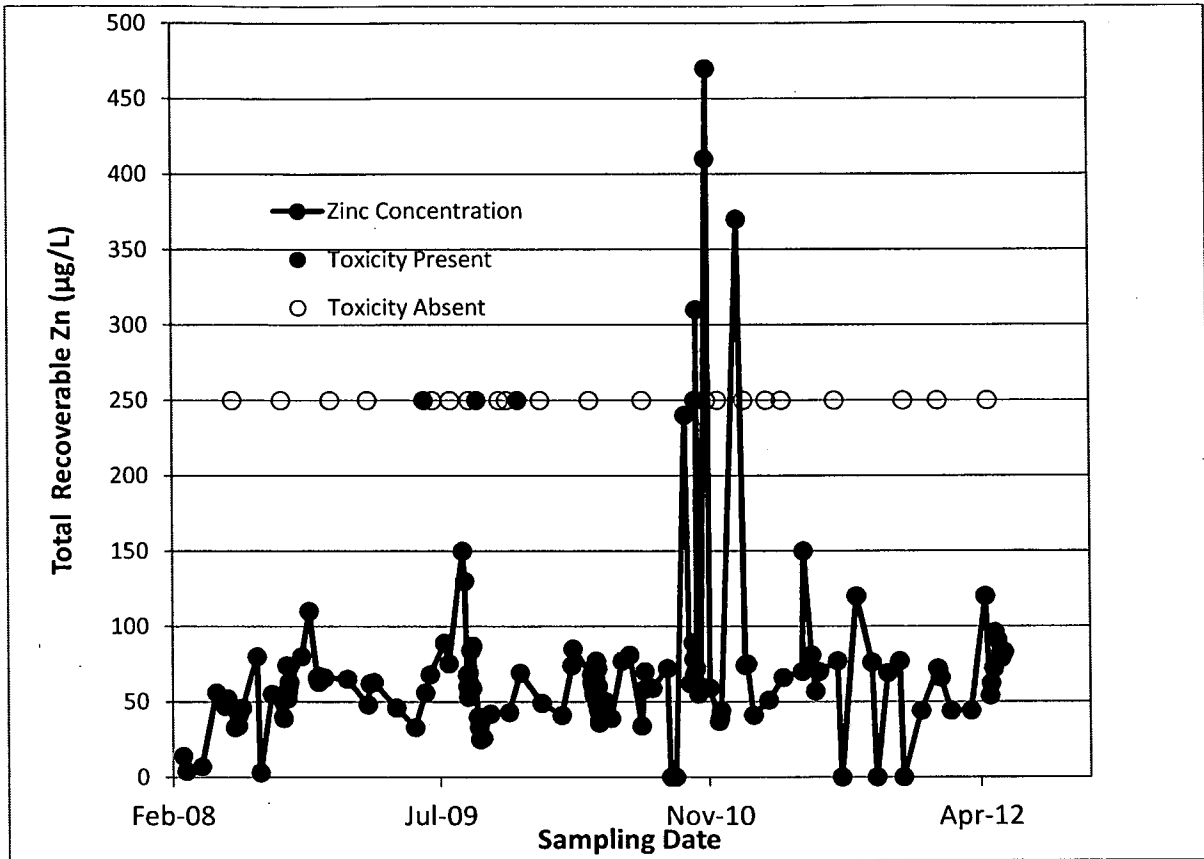


Figure 1.1. Plot of zinc concentrations and occurrences of WET excursions.

A summary of exceedance factors (measured zinc concentration ÷ permit limit) for recent (January 2010 through September 2011) routine monitoring data is presented in Table 1.4. The 95th percentile values for the exceedance factors corresponding to the monthly average and weekly average permit limits are 1.9 and 1.0, respectively. This result indicates that the existing monthly average permit limit would need to be increased by a factor of approximately 1.9 to result in permit compliance. The discharge is in general compliance with the weekly maximum permit limit.

Table 1.4. Summary of zinc concentrations and exceedance factors for January 2010 through September 2012.

Summary Statistic		Value (µg/L)	Exceedance factor	
			Monthly Average (85.5 µg/L)	Weekly Average (171.6 µg/L)
Percentile	95	163.9	1.9	1.0
	75	84.8	1.0	0.5
	50	69.0	0.8	0.4
	25	48.4	0.6	0.3
Minimum		40.0	0.5	0.2
Average		79.6	0.9	0.5
Maximum		249.8	2.9	1.5
Proportion exceeding permit limit			0.12	0.04

1.4 Proposed Approach

Technical guidance for conducting a WER study is provided in US Environmental Protection Agency's (EPA) Interim Procedure (EPA 1994), which applies to most metals. Accordingly, WER testing for Van Buren will be conducted according to EPA (1994).

The proposed approach will use "Method 1" in EPA (1994). This method can be used to determine a WER in the vicinity of a plume or in receiving streams with zero flow (EPA 1994). The critical flow for Outfall 001 is 100%. Therefore effluent samples will not be mixed with water collected from the receiving stream.

For each sample collected for WER determination, the following metal-spiked sample matrices will be tested concurrently:

1. Laboratory water prepared per EPA (1991), and
2. 100% effluent.

Average effluent hardness from routine biomonitoring is 220 mg/L. Accordingly, the hardness of the laboratory water test will be 200 mg/L, subject to the restrictions given in Section F.3 of EPA (1994). To compare the laboratory water and site water LC50s (i.e., the simulated downstream mixture) for purposes of WER calculations, the site water LC50s will be normalized to the hardness of the laboratory water using the following formula:

Formula 1.1.

$$LC50_{at\ Lab\ Hdns} = LC50_{at\ Sample\ Hdns} \left[\frac{Lab\ Hdns}{Sample\ Hdns} \right]^S$$

Where: **LC50_{at Lab Hdns}** = LC50 of site water (effluent or simulated downstream sample) normalized to lab water hardness,
LC50_{at Sample Hdns} = LC50 of effluent test or simulated downstream sample test,
Lab Hdns = hardness of water used in laboratory water test,
Sample Hdns = hardness of effluent or simulated downstream sample, and
S = the log-log slope of the hardness regression for zinc = 0.8473 per Appendix B of EPA's National Recommended Water Quality Criteria¹.

This approach is consistent with the use of hardness adjustments given in the Interim Procedure (EPA 1994; Method 1, Section A.6).

¹ <http://water.epa.gov/scitech/swguidance/standards/current/index.cfm#appendxb>

WERs are known to be affected by water quality parameters that vary seasonally (e.g., hardness, pH, organic carbon). Accordingly, sampling for WER testing will be conducted during late summer/early fall low flows (September and October), winter flows (December and January) and spring high flows (May and June).

2.0 SAMPLING AND TESTING PROTOCOL

The following sampling and testing protocol is based on Method 1, Section D through H of EPA (1994). All toxicity test procedures and analytical testing will be conducted by American Interplex Corporation (AIC), which is certified by the Arkansas Department of Environmental Quality (ADEQ). Per EPA (1994), definitive tests used for WER determination will be conducted on three occasions using samples collected at least 3 weeks apart. Specifically sampling will be conducted during late summer/early fall low flows (September and October), winter flows (December and January), and spring high flows (May and June).

An initial range-finding test will be conducted to identify the concentration range to be used and to evaluate the need for daily renewals in subsequent tests. The first of the three definitive tests will be conducted using both *Ceriodaphnia dubia* and *Pimephales promelas*. Subsequent definitive tests will use the more sensitive species as indicated by the first definitive test².

2.1 Test Organisms

The test organisms used for this testing will be *C. dubia* and *P. promelas*. These test organisms are used for Van Buren's routine biomonitoring, and their use for WER determination is consistent with recommendations in Appendix I of EPA (1994). Water chemistry collected during routine biomonitoring tests suggest that the hardness, alkalinity, and pH do not differ greatly between the site water and the culture water used by AIC. *C. dubia* used in testing will be < 24 hours of age at the beginning of the test. Test organisms will be fed algae before they are transferred to the test chambers to begin the test. However, no food will be placed in the test containers, and special care will be taken to prevent the transfer of food to the test containers along with the test organisms when the test is loaded. *P. promelas* used in testing will be 1 to 24 hours of age at the beginning of the test. Test organisms will be hatched in laboratory

² Data presented in Table 1 of EPA (1980) indicate that *C. dubia* and *P. promelas* fry 1 – 24 hours of age might show similar sensitivity to zinc. Therefore it is possible that definitive WER testing might be performed using *P. promelas*.

dilution water and will not be fed before or during the test. At least 90% of the *P. promelas* fry used in the test must survive in laboratory water for at least 6 days after hatching.

2.2 Sample Collection

A 24-hour composite sample of effluent will be collected using an automated sampler from the NPDES compliance point. Sampler bottles will be washed according to AIC QA Plan specifications (detergent-washed, rinsed in acid+deionized water). Samples to be used for toxicity testing will be maintained unpreserved at 1°C to 4°C during collection, shipment, and storage. The flow-weighted composite sample will be prepared in the laboratory using flow data provided by Van Buren personnel. Sub-samples of the composite will be collected for analysis of chemical parameters using appropriate sample-container cleaning and sample preservation. Samples will be stored in the dark at 1°C to 4°C with no headspace in the container.

The effluent sample will be collected during normal plant operating conditions. Normal operating conditions will be documented based on measurements of DMR monitoring parameters listed in Table 1.3 and flows taken during the time of effluent sampling, and then compared with values typical for the plant. Sample delivery to the testing laboratory will include appropriate completed chain-of-custody documentation. EPA (1994) stipulates that upstream samples "... **must not** be unduly affected by runoff events that cause higher levels of TSS than would normally be present, unless there is particular concern about such conditions." Since the winter and spring samples are intended to evaluate the WER at higher flows, upstream samples will at times be influenced by runoff. However, sampling will not occur during major runoff events.

2.3 Laboratory Test Water

Water used in the laboratory water toxicity tests will be prepared per EPA (1991). The concentration of total organic carbon (TOC) and TSS in the laboratory water will be < 0.5 mg/L and < 4 mg/L, respectively. The concentration of salts used to prepare the laboratory water will be adjusted to provide a hardness of 200 mg/L. This approach will result in laboratory water with

levels of alkalinity and pH that are between 40 mg/L and 220 mg/L, and similar to the site water per EPA requirements (EPA 1994).

2.4 Toxicity Tests

2.4.1 Range-Finding Tests

Range-finding tests will be conducted prior to the definitive toxicity tests used to calculate the WER. The purpose of the range-finding test is to determine the appropriate range of zinc concentrations for the definitive tests and to indicate whether or not the definitive tests can be conducted as static renewal or static non-renewal tests. The range-finding tests can also provide a preliminary estimate of the WER. Range-finding tests will be conducted on effluent/receiving stream mixture and laboratory water spiked with inorganic zinc salts.

The zinc stock solution used to spike the effluent/receiving stream mixture and laboratory water will be prepared from deionized water and reagent-grade zinc chloride ($ZnCl_2$). The stock solution will be sufficiently concentrated to prevent significant dilution of the effluent or laboratory water with the deionized water matrix. The stock solution will be sufficiently acidified with reagent-grade acid to prevent zinc precipitation during storage, while not containing excess acid that will affect the pH of the test solutions.

Testing will consist of 48 static non-renewal tests using ten organisms per concentration and up to eight zinc exposure concentrations. Because the purpose of the range-finding test is to determine the appropriate upper and lower ranges of zinc concentrations for the definitive tests, a dilution factor of 0.3 will be used and zinc concentrations will not be measured at each exposure concentration. However, initial and final zinc concentrations will be measured at selected concentrations to evaluate the change in zinc concentration occurring in the test beakers during the test.

2.4.2 Definitive Tests

Definitive toxicity tests to be used for the calculation of the WER will be designed based on the results of the range-finding tests. Tests will be conducted as static renewal tests if the range-finding tests indicate there will be greater than a 50% decrease in dissolved zinc

concentration between the initial and final values or an unacceptable decrease in DO in the test beakers.

A dilution factor of at least 0.65 will be used to establish the zinc concentrations in successive test exposures. For purposes of preparing this protocol, it is assumed that static renewal tests will be required. The procedure for the static non-renewal test will be essentially identical except for the intervening renewal step. Definitive tests will be conducted using a freshly collected effluent sample. Testing will begin within 36 hours of sample collection. Exposure solutions will be prepared by preparing a large volume of the highest test concentration of effluent and laboratory water. Serial dilutions of the spiked effluent and laboratory water will be prepared using unspiked portions of the effluent and laboratory water, respectively, as diluent. The same zinc stock solution (prepared as stated above) will be used to spike both effluent and laboratory water samples. The mixed solutions will then be allowed to equilibrate at test temperature for 1 to 3 hours.

After the equilibration period, appropriate volumes of exposure solution (per EPA 1991) will be dispensed into the test chambers. Aliquots of these initial test solutions will be retained for zinc analysis as described in following sections. Test organisms will be assigned randomly or impartially to the test chambers. Five test chambers, each containing five organisms, will be used for both the effluent/receiving stream and laboratory water tests. Four of the chambers will serve as the actual experimental chambers that will provide the counts of surviving organisms. The fifth chamber of each test concentration will be used as a "chemistry control." Routine test measurements such as temperature, DO, and pH will be taken from the chemistry controls to reduce the possibility of cross-contamination of test solutions due to the use of instrument probes during routine test maintenance. Test organisms for both the effluent and the laboratory tests will be added at the same time (within 0.5 hour). The two tests (effluent/receiving stream and laboratory water) will then be conducted so that there are no differences other than the composition of the water matrix and the zinc concentrations. Tests will be maintained and test organism effects/symptoms will be observed and recorded as specified in EPA (1991).

For test solution renewal at 24 hours (if needed), a fresh set of exposure solutions will be prepared and transferred to clean test chambers in the same way as described above. Aliquots of

the new solutions will be retained for the analysis of zinc as described in Section 3.0. Test organisms from the old solutions will then be transferred to the new solutions using a pipette. Old solutions from each exposure will be combined into a single aliquot for each test exposure for zinc analysis as described in Section 3.0.

For non-renewal tests, aliquots of the test solutions will be retained for the analysis of total dissolved zinc at the beginning and at the end of the test as described in Section 3.0.

3.0 CHEMICAL AND OTHER MEASUREMENTS

Effluent samples collected for each series of tests (including range-finding tests and definitive tests) will be analyzed for the parameters listed in Table 3.1. This parameter list includes routine NPDES permit parameters that are analyzed to document plant operating conditions.

Table 3.1 Analytical parameters for effluent, upstream, and simulated downstream samples to be collected for WER testing.

Parameter	Analytical Method	Reporting Limit (mg/L)
Total Recoverable Copper *	EPA 200.8	0.006
Dissolved copper *	EPA 200.8	0.006
Total Recoverable Zinc *	EPA 200.8	0.006
Dissolved Zinc *	EPA 200.8	0.006
Fecal Coliform Bacteria	SM 9221, 9222	10 CFU/100mL
pH **	HydroLab meter	Not applicable
Dissolved Oxygen **	HydroLab meter	0.5
Temperature **	HydroLab meter	Not applicable
Total Organic Carbon *	EPA 415.1	1.0
Hardness*	EPA 130.0	1.0
Total Alkalinity*	EPA 310.0	10
Dissolved Organic Carbon *	EPA 415.1	1.0
TSS *	EPA 160.2	4.0
CBOD5 *	EPA 405.1	2.0

*Parameters also to be measured in laboratory water.

** Measured in effluent at the time of sample arrival to the laboratory.

Samples for the analysis of zinc will be collected from each concentration at the beginning and end of each 24-hour period. The sample for the end of a 24-hour period (and/or end of the test, as appropriate) for a particular test concentration will be collected by combining all four replicates into a single composite. A portion of the composite will then be filtered through a 0.45 µ membrane filter. The preserved zinc samples will be analyzed as a single batch at the end of the test. Analyses will be conducted only on those concentrations necessary for LC50 calculations.

4.0 DATA QUALITY OBJECTIVES

Toxicity testing, analytical procedures, and results will undergo Quality Assurance/Quality Control (QA/QC) review as specified in AIC's written QA/QC procedures. Toxicity test acceptance criteria are summarized in Table 4.1. Acceptance criteria for chemical analyses are provided in Table 4.2. Toxicity tests that do not meet acceptance criteria will not be considered valid for the study purposes. Chemical analyses that do not meet acceptance criteria will be repeated, if possible. The need to invalidate testing based on failure to meet acceptance criteria for chemical analyses will be determined, with agency consultation, based on the type and severity of the failure. Toxicity and analytical tests may also be invalidated for additional reasons identified during the routine QA/QC review performed by AIC.

Table 4.1. Acceptance criteria for toxicity tests.

Test Parameter	Acceptance Criterion
Temperature	25°C ± 1°C ¹
DO	> 6 mg/L in all test concentrations ²
pH	6.5 – 8.5 su ²
Performance control survival	≥ 90% ^{1,3}
Unspiked effluent control	≥ 90% ³
Percent decrease in dissolved metal concentration between initial and final measurements	< 50% ³
Percent of adversely affected organisms in laboratory water test	> 50% in at least one test concentration ³
Percent of adversely affected organisms in effluent test	< 50% in at least one test concentration ³
Dose response	Inverted dose response does not affect more than two concentrations having between 20% and 80% mortality ³

Notes:

1. Based on EPA (1991).
2. Based on typical levels observed during routine biomonitoring.
3. Based on EPA (1994).

Table 4.2. Acceptance criteria for chemical analyses.

Analytical Parameter	Analytical Method	Quality Control Parameter		
		Duplicate RPD	LCS % Recovery	Laboratory Blank (mg/L)
Dissolved Copper	EPA 200.8	+ 20%	NA	<0.006
Total Zinc	EPA 200.8	+ 20%	85 - 115%	<0.006
Dissolved Zinc	EPA 200.8	+ 20%	NA	<0.006
Total Organic Carbon	EPA 415.1	+ 20%	85 - 115%	<1.0
Dissolved Organic Carbon	EPA 415.1	+ 20%	NA	<1.0
Total Alkalinity	EPA 310.0	+ 20%	N/A	<1.0
Hardness	EPA 130.0	+ 20%	85 - 115%	<1.0
TSS	EPA 160.2	+ 20%	NA	<4.0
BOD ₅	EPA 405.1	+ 20%	NA	<2.0

5.0 CALCULATING AND INTERPRETING RESULTS

LC50 values will be calculated using probit analysis or computational interpolation (e.g., trimmed Spearman-Kärber) using time-weighted average concentrations if the data allow. LC50 and WER computations will be carried out to at least four significant digits to avoid rounding errors.

The measurement of both total and dissolved zinc in the tests will allow calculation of both a total and dissolved WER. Given the approach used by ADEQ to establish permit limits, it is likely that the site-specific WER will be calculated as a dissolved WER with the subsequent use of the translator to convert the criterion to a total concentration. Regardless of whether the final site-specific WER is based on total or a dissolved concentration, the calculation of the WER is the same. WER calculation per EPA (1994) will be as follows:

1. Normalize the LC50s from the laboratory water and the site water to the same hardness using Formula 1.1;
2. Calculate the sample WER from LC50 values normalized to the same hardness by dividing the hardness-normalized site water LC50 by the hardness-normalized laboratory water; and
3. The final site WER is then calculated as the geometric mean of the three sample WERs from separate samples collected at least 3 weeks apart.

6.0 REPORTING THE RESULTS

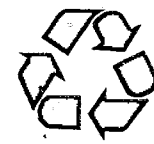
A report of the results will be prepared containing, at a minimum, the information required by Method 1, Section J, EPA (1994). The report will include summary tables that identify the measured total and dissolved zinc concentrations in each test solution aliquot (laboratory water, simulated downstream water, and 100% effluent) at test initiation and test termination (and during any renewals), along with percent survival for each of the WER tests conducted. The report will also include appendices with copies of the sample custody reports, the bioassay data sheets, the laboratory analytical reports, and the statistical analysis inputs/outputs.

7.0 LITERATURE CITED

- APCEC. 2011. *Regulation No. 2: Regulation establishing water quality standards for surface water of the State of Arkansas*. Arkansas Pollution Control and Ecology Commission. Effective December 3, 2010.
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- EPA. 1991. *Methods for Measuring the Acute Toxicity of Effluent and Receiving Waters to Freshwater and Marine Organisms, Fourth Edition* [EPA/600/4-90/027]. US Environmental Protection Agency, Office of Research and Development. Washington, DC, September 1991.
- EPA. 1994. *Interim Guidance on Determination and Use of Water-Effect Ratios for Metals* [EPA-823-B-94-001]. US Environmental Protection Agency, Office of Water. Washington, DC. February 1994.


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