Proposed Site-Specific Copper Criteria for the City of Idabel Discharge to Mud Creek

Oklahoma Water Resources Board
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INTRODUCTION

Oklahoma's Water Quality Standards (WQS) include copper criteria to protect aquatic life from copper toxicity. However, copper toxicity can be influenced by a variety of site-specific water quality conditions and thus the WQS provide for the development of site-specific criteria. This staff report provides pertinent background information regarding the proposed site-specific copper criteria for the City of Idabel discharge to Mud Creek.

BACKGROUND

REGULATORY AUTHORITY

The Oklahoma Water Resources Board's statutory authority and responsibility concerning establishment of standards of quality of waters of the state are provided for under 82 O.S., §1085.30(A). Under this statute the Oklahoma Water Resources Board is authorized to promulgate rules *which establish classifications of uses of waters of the state, criteria to maintain and protect such classifications, and other standards or policies pertaining to the quality of such waters*. These Standards are designed to maintain and protect the quality of the waters of the state. Standards are comprised of three components 1) a waterbody's beneficial uses, 2) water quality criteria to protect those uses and determine if they are being attained, and 3) antidegradation policies to help protect high quality waters. Oklahoma's Water Quality Standards, which work to safeguard human health and aquatic life, are contained in OAC 785:45 and include copper criteria to protect aquatic life from copper toxicity.

WATER CHEMISTRY AND COPPER BIOAVAILABILITY

Copper is a naturally occurring trace element and an essential micronutrient for plants and animals. Copper in surface water may be a product of local geologic weathering processes with reported background concentrations ranging from 0.2 µg/L to 30 µg/L in contrast to concentrations as high as 100 µg/L in waters impacted by anthropogenic inputs (Nriagu 1979; Bowen 1985; Hem 1989). Sources of copper due to pollution include mining, leather processing, fabricated metal and electrical equipment manufacturing, as well as, municipal wastewater treatment plants (Patterson et al. 1998).

Copper bioavailability and subsequent toxicity is mediated by water chemistry. Copper bioavailability to aquatic organisms varies because it exists in different forms or chemical species, some of which are more easily taken up by organisms. Copper is highly reactive with both inorganic and organic chemicals in surface waters and binds to other molecules and form complexes or ligands and is readily sorbed onto surfaces of suspended solids. Physiochemical characteristics of the water that have been known to impact copper speciation and bioavailability in surface waters include temperature, dissolved organic carbon, total suspended solids, pH, hardness, and alkalinity (EPA 2003).

OVERVIEW OF STATEWIDE COPPER CRITERIA

Aquatic life criteria address the state's goals of providing for the protection and propagation of fish and wildlife. Aquatic life criteria for toxic parameters are determined based on the results of toxicity tests with aquatic organisms in which unacceptable effects on growth, reproduction, or survival occurred. Criteria are designed to be protective of the majority of species in an aquatic community. Numerical criteria to protect beneficial uses including fish and wildlife propagation, from toxic substances are found in OAC 785:45, Appendix G, Table 2. These criteria are organized into toxic organics and toxic inorganics, which are primarily metals. Because of the relationship between the bioavailability of metals and water chemistry, especially water hardness, to adequately protect aquatic life, the majority statewide acute and chronic criteria to protect aquatic life from effects of metals are expressed as equations that account for ambient water hardness (Table 1).

The equations were derived using a linear regression analysis of the relationship between copper toxicity to aquatic organism and water hardness ($CaCO_3$). Although there is a strong correlation between them, there are some limitations to the analysis because the observed relationship may not be solely due to hardness, but to constituents that are usually correlated with hardness such as alkalinity and pH (Erickson et al. 1994; Mayer et al. 1994). As such, hardness is a surrogate for other water quality parameters and the resulting equations are most accurate when applied to waters with water quality conditions in the range of those used in the regression analysis (25-400 mg/L $CaCO_3$) but may be applied to waters outside that range with special considerations (EPA 1997; EPA 2000). The hardness of surface waters across Oklahoma vary widely with stream segment means as low as 18.76 mg/L in the southeast to as high as 2095 mg/L in the southwest (OAC 785:46, Appendix B). Thus, it is necessary that the statewide criteria account for local or site-specific hardness conditions. In the absence of site-specific hardness values, mean stream segment hardness (mg/L $CaCO_3$) in OAC 785:45, Appendix B are used to calculate the criterion.

TABLE 1. OKLAHOMA'S STATEWIDE COPPER CRITERIA FOR THE PROTECTION OF AQUATIC LIFE

	Acute (µg/L)	Chronic (µg/L)
Statewide	e(0.9422[ln(hardness)]-1.3844	e(0.8545[ln(hardness)]-1.386
Mud Creek*	6.56	4.83

*Calculated using mean stream segment hardness of 32 mg/L $CaCO_3$ (OAC 785:46, Appendix B)

Oklahoma's metals criteria are in the dissolved metal form because this is the more bioavailable fraction of the metal in the water column compared to the total recoverable metal (EPA 1996). However, permits issued as part of Clean Water Act (CWA) programs such as the Oklahoma Pollutant Discharge Elimination System, are required to set permit limits based on total recoverable metals because of the uncertainty in the difference in bioavailability of a metal in the effluent and receiving water (40 CFR 122.45). Therefore, there are conversion factors for total-to-dissolved metal fractions, derived using the percent dissolved metals measured across a broad range of analytical tests (EPA 1996), found in 785:45, Appendix G, Table 3. In addition, dischargers may utilize options available in OWQS to develop site-specific criteria by modifying the state-wide hardness based criteria.

SITE-SPECIFIC COPPER CRITERIA DEVELOPMENT

Statewide criteria can be modified to reflect site-specific conditions and Oklahoma Water Quality Standards provide for the development of site-specific criteria (785:45-5-4(g) and Appendix E). There are three options in OAC 785:45, Appendix E(E) available to permittees wanting to pursue the development of site-specific criteria for metals, 1) a water effects ratio (WER), 2) a dissolved to total translator, and 3) the combination of the two. A water effects ratio (WER) is a tool which provides for allowance at the point of discharge and may be used alone or in combination with a site-specific total-to-dissolved translator. A WER accounts for the difference between the toxicity of a metal in the site water and the toxicity of a metal in laboratory water.

In 2001, EPA released the "*Streamlined Water-Effect Ratio Procedure for Discharges of Copper*" which provides an easier and more efficient approach to obtain the data needed derive a WER for copper compared to the "*1994 Interim Guidance on Determination and Use of Water-Effect Ratios for Metals*". However, the scope of applicability is narrowed as the streamlined procedure is only recommended when elevated copper concentrations are due to continuous point sources. The streamlined procedure includes experimental design, data collection and data analysis requirements to follow when conducting a WER study (Table 2). Two sampling collections of upstream and effluent must be performed at least one month apart during stable flow conditions while plant performance is average or better with CBOD (carbonaceous biochemical oxygen demand) and suspended solids concentrations within permit limits. Water quality should be similar to times when nonpoint source inputs of organic matter and suspended solids are relatively low. *Ceriodaphnia dubia* or *Daphnia magna* were chosen to be the most suitable for these tests because they are sensitive to copper, have been the most useful test organisms for WER studies and have a substantial amount of EC50 laboratory data.

The streamlined WER guidance and OWRB's, "*Guidance for Developing Site Specific Criteria for Metals*" (2003) must be followed when developing a WER for copper in Oklahoma. The streamlined procedure differs from OWRB's guidance in several ways (Table 2) which reduce sampling and calculation efforts – i.e. two minimum sampling events in the streamlined guidance vs. three in the OWRB guidance. One key difference is the preparation of site water. In the streamlined procedure, the mix of effluent and upstream samples is the design low-flow dilution ratio instead of the dilution ratio at the time of sampling in the OWRB procedure. Another difference is the calculation of the WER's. OWRB's equations for the WER is the reciprocal of the streamlined procedures and the streamlined procedure includes the addition of using the SMAV or lab water (LW) LC50, which helps to ensure that the resulting WER is conservative. Modifications in lab and field requirements stem from experience with the interim procedure showing the additional steps do not add value in these specific cases. Limiting the scope of the procedure application to only well understood situations results in a more efficient and predictable procedure. The changes in design in the streamlined procedure from the 1994 interim procedure were assessed for aquatic life protectiveness and comparability using the Monte Carlo probabilistic modeling. The analysis concluded the streamline procedure to be inherently less subject to random sampling variability, so fewer samples are still reliable, and the two procedures yielded similar results (EPA 2001).

TABLE 2. REQUIREMENTS OF WATER EFFECT RATIO STUDIES FOR DISCHARGES OF COPPER

Requirement	2003 OWRB Guidance	2001Streamlined Guidance
Applicability	All metals any source	Continuous point source copper
Min. sampling events	3	2; 1 month apart
Min. WER's	4	2
Min. WER's in fWER	3	2
Site Water mix	Dilution at sampling	Design low flow dilution ratio
Plant operation	Must be representative of normal operation	Average or better, CBOD and TSS within permit limits
Chemical Analyses	Total and Dissolved Copper, Hardness, pH, Alkalinity, TSS, TOC, TDS	Total and Dissolved Copper, Hardness, pH, Alkalinity, TSS, TOC, TDS
Toxicity testing	Several acceptable	Side by side, 48hr LC50
Species in toxicity test	2; different orders	1; *Cerodaphnia dubia* or *Daphnia magna*
WER calculation*	LW LC50/SW LC50	SW LC50/ Lesser of LW LC50 or SMAV
Final WER calculation	$1/\exp[\sum \ln(WER_i)/n]$	$\exp[\sum \ln(WER_i)/n]$

*LW is lab water, SW is site water, SMAV is species mean acute value, LC50 is the lethal concentration required to kill 50% of the test population

SITE-SPECIFIC CRITERIA EQUATIONS

In order to modify the existing statewide criteria, a WER that has been derived using the guidance and equations in Appendix E is applied to the statewide hardness based criterion that has been calculated using the equations in OAC 785:45, Appendix G, Table 2 and mean segment hardness in OAC 785:46, Appendix B.

Options Allowed In Appendix E:

1. Water Effects Ratio	2. Dissolved to Total Translator	3. Combining f and fWER
$S_{ast} = C_{ast}/FWER_t$	$S_{ast} = C_{csd}/f$	$S_{ast} = C_{asd}/(fxFWER_d)$
$S_{cst} = C_{cst}/FWER_t$	$S_{cst} = C_{csd}/f$	$S_{cst} = C_{csd}/(fxFWER_d)$

C_{ast} = acute statewide total criterion
C_{cst} = chronic statewide total criterion
C_{asd} = acute statewide dissolved criterion
C_{csd} = chronic statewide dissolved criterion
S_{ast} = acute site-specific total criterion
S_{cst} = chronic site-specific total criterion
$FWER_t$ = final total water effects ratio
$FWER_d$ = final dissolved water effect ratio
f = dissolved to total fraction

CITY OF IDABEL AND MUD CREEK

The City of Idabel has a population of 7,010 (U.S. Census 2010) and is located in McCurtain County in Southeastern Oklahoma. The publicly owned treatment works (POTW) is located south of the city and discharges to Mud Creek (Figure 1). The POTW design flow is 2.56 cfs (1.65 MGD) and the background flow rate of Mud Creek is the default 1 cfs (0.6463 MGD). The critical dilution of 100% effluent used in the WER study is the same used in OPDES permitting copper limit calculations and the whole effluent toxicity (WET) testing requirement. Mud Creek flows east and north past the discharge point to its confluence with the Little River. The current statewide hardness based criteria (chronic- 4.83 µg/L and acute- 6.56 µg/L) are calculated using a hardness of 32.0 mg/L $CaCO_3$, which is the mean hardness value for the nearest water segment (410200) in Chapter 46, OWQS Implementation, Appendix B. The workplan and submitted by GBM[c] & Associates on behalf of the City of Idabel stated the POTW had not consistently achieved their permitted copper concentration limits in their discharge (7.94 µg/L daily maximum, 3.96 µg/L monthly average, total recoverable copper). Therefore, Idabel developed a WER and dissolved translator in an effort to maintain compliance with their OPDES permit (GBM[c] & Associates 2017).

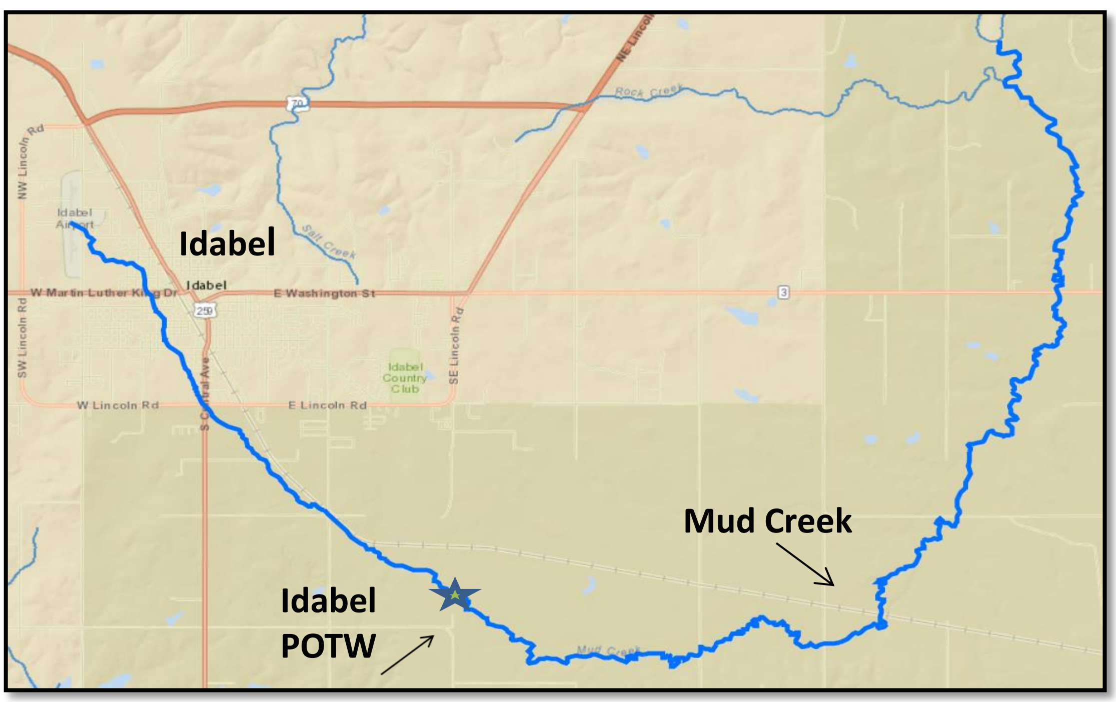

FIGURE 1. LOCATION OF CITY OF IDABEL POTW DISCHARGE TO MUD CREEK

WATER EFFECTS RATIO STUDY SUMMARY

The City of Idabel (OPDES Permit No. OK0027677, effective November 1, 2012) submitted a workplan on April 21, 2015 and was approved by OWRB staff on July 15, 2015. The WER and dissolved translator samples were collected in 2016 from May to September. The dissolved translator was developed by calculating the geometric mean of eleven dissolved and total copper measurements (Figure 3). On July 26, 2016 and September 27, 2016 four grab samples per WER test were collected over a 6 hour period and composited and used to conduct acute 48-hour static non-renewal dissolved and total copper toxicity tests with *Cerodaphnia dubia*. An example of the calculations involved in the development of the site-specific copper criteria using the values measured during this study are found in the following section (Example 1) and a summary of the toxicity testing and dissolved translator results and calculations taken directly from the WER study final report are in Appendix A.

The LC50's obtained from the each of the four site water (SW) WER tests (two dissolved copper, two total copper) were normalized to the respective lab water (LW) hardness (Figure 2). The normalized LW LC50's were compared to normalized species mean acute value (SMAV; geometric mean of the *Cerodaphnia dubia* LC50's used during the derivation of the statewide copper criteria) and the lesser of the two were used in the calculation of the WER. The dissolved copper WER's were less than the total copper WER's for both sampling dates and therefore were used in the calculation of the fWER (geometric mean of WER's) because they were the most conservative (Figure 2 and 3). The proposed criteria were derived using the combination of the WER and dissolved translator option (OAC 785:45, Appendix E). The current statewide acute and chronic dissolved criteria were divided by the criterion translator (fWER*dissolved translator) to get the final modified copper criteria for the City of Idabel discharge to Mud Creek. The final copper WER study report submitted by the City of Idabel was found to follow the workplan and meet all of the guidance requirements and was approved by OWRB staff on September 1, 2017.

EXAMPLE 1. SITE-SPECIFIC CRITERIA CALCULATION

Dissolved Copper Toxicity Test Results

Test #1 LC50's	**Test #2 LC50's**
Lab Water: 6.66	Lab Water: 6.62
Site Water: 105	Site Water: 108

Hardness normalized LC50's

SW LC50 (LW hardness/SW hardness) $^{0.9422}$

Test #1 normalized SW LC50: 105 x (98000/77000)$^{0.9422}$=131.8 µg/L
Test #2 normalized SW LC50: 108 x (89000/69000)$^{0.9422}$=137.3 µg/L
Test #1 normalized SMAV: 22.11 x (98000/100000)$^{0.9422}$=21.7 µg/L
Test #2 normalized SMAV: 22.11 x (89000/100000)$^{0.9422}$=19.8 µg/L

Water Effects Ratio's

Lesser of LW LC50 or SMAV/SW LC50

WER 1: 21.7/131.8= 6.08
WER 2: 19.8/137.3= 6.93

fWER

1/exp [$\sum \ln(WER_i)/n$]

exp [ln(6.08)+ln(6.93)/2]=6.49
(1/6.49)=0.1541

acute site-specific total criterion
6.56/(0.75)(0.1541)= 54.28

chronic site-specific total criterion:
4.83(0.75)(0.1541)= 39.97

PROPOSED SITE-SPECIFIC COPPER CRITERIA

The language below is the proposed site-specific criteria to be inserted into OAC 785:45, Appendix E(F) Site-Specific Criteria for Metal Which Have Been Developed for Particular Waterbodies. These criteria will be added to the existing site-specific criteria for the City of Idabel Discharge to Mud Creek that have been previously promulgated.
OAC 785:45, Appendix E(F)(3)(D) shall read:

3. City of Idabel Discharge to Mud Creek at SW 1/4 of SW 1/4 of SW 1/4 of Section 15, T 8 S, R 24 EIM, McCurtain County, Oklahoma (Latitude 33° 51’ 14.621” North, Longitude 94° 47’ 22.200” West)

D. Copper

A site-specific criteria modification study has been satisfactorily completed for copper for the City of Idabel discharge to Mud Creek. All criteria are calculated at an in-stream hardness of 32 mg/L.

$FWER_t$ = 0.1409
$FWER_d$ = 0.1541
f = 0.7527

The results of the study allow any of the four following criteria to be utilized.

C_{cst} = 4.83 µg/L	Statewide criterion
S_{cst} = 31.34 µg/L	Option 1
S_{cst} = 6.16 µg/L	Option 2
S_{cst} = 39.97 µg/L	Option 3
C_{ast} = 6.56 µg/L	Statewide criterion
S_{ast} = 42.56 µg/L	Option 1
S_{ast} = 8.37 µg/L	Option 2
S_{ast} = 54.28 µg/L	Option 3

REFERENCES

Bowen, H.J.M. 1985. In D. Hutzinger (ed.), The Handbook of Environmental Chemistry, Vol. 1, Part D: The natural environment and biogeochemical cycles, Springer-Verlag, New York. p. 1-26.

GBMc & Associates. 2017. Water Effects Ratio Study Final Report for the City of Idabel, OK. Bryant, AR. http://www.owrb.ok.gov/util/rules/wqs_revisions.php

Hem, J.D. 1989. Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geological Survey water-supply paper 2253. Government Printing Office.

Nriagu, J.O. (Ed.) 1979. Copper in the Environment. Part I: Ecological Cycling; Part II: Health Effects. Wiley and Sons, Inc. New York, NY.

Office of Administrative Rules. Classification of water uses - Oklahoma Water Quality Standards. Oklahoma Statutes. Title 82. Water and Water Rights (82 O.S., §1085.30(A)) Oklahoma City, OK.

Office of the Federal Register. Calculating NPDES Permit Conditions. Code of Federal Regulations, Title 40 Chapter I Subchapter D, Part 122 (40 CFR 122.45) Washington, D.C.

Oklahoma Water Resources Board. 2003.Guidance for Developing Site Specific Water Quality Criteria for Metals, OWRB Technical Report TRWQ2002-1. Oklahoma City, OK.

Oklahoma Water Resources Board. 2017a. Oklahoma Water Quality Standards, Chapter 45, OAC 785:45. Oklahoma City, OK.

Oklahoma Water Resources Board. 2017b. Implementation of Oklahoma Water Quality Standards, Chapter 46, OAC 785:46. Oklahoma City, OK.

Patterson, J.W., R.A. Minear, E. Gasca and C. Petropoulou. 1998. Industrial discharges of metals to water. In: H.E.Allen, A.W. Garrison and G.W. Luther III (Eds.). Metals in Surface Waters. Ann Arbor Press, Chelsea, MI. pp. 37-66.

Stephen, C., Mount, D., Hansen, D., Gentile, J., Chapman, G., and W. Brungs. 1985. EPA Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses (PB85-227049). United States Environmental Protection Agency, Washington, D.C.

United States Census Bureau. 2010. "Idabel Oklahoma QuickFacts". https://www.census.gov/quickfacts/fact/table/idabelcityoklahoma/PST045216 (11 November 2017).

United States Environmental Protection Agency (EPA).1994. Interim Guidance on Determination and Use of Water-Effect Ratios for Metals (EPA-823-B-94-001). Washington, D.C.

United States Environmental Protection Agency (EPA). 1996. The metals translator: draft guidance for calculating a total recoverable permit limit from a dissolved criterion. U.S. EPA, Exposure Assessment Branch, Washington D.C.

United States Environmental Protection Agency (EPA). 1997. Use of the WER Procedure with Hardness Equations. U.S. EPA Health and Ecological Criteria Division, Washington, D.C.

United States Environmental Protection Agency (EPA). 2000. Federal Register Part III. Water Quality Standards; Establishment of Numeric Criteria for Priority Pollutants for the State of California

United States Environmental Protection Agency (EPA). 2001. Streamlined Water-Effect Ratio Procedure for Discharges of Copper (EPA-822-R-01-005) Washington, D.C.

United States Environmental Protection Agency (EPA). 2007. Aquatic Life Ambient Freshwater Quality Criteria—Copper 2007 Revision (EPA-822-R-07-001). Washington, D.C.

APPENDIX A

WER 1-JULY 26, 2016

Effluent Hardness (µg/L)	69000
Lab water Hardness (µg/L)	89000
Total Copper SMAV (µg/L)	24
Normalized SMAV	21.5
D. Copper SMAV (µg/L)	22.11
Normalized SMAV	19.8

Total Copper - Ceriodaphnia

	LC50 (µg/L)	Normalized LC50
Effluent	125	158.9
Lab Water	7.17	7.17

*Normalized LC50 = SWM LC50 x (lab hdns/swm hdns)^0.9422

Dissolved Copper - Ceriodaphnia

	LC50 (µg/L)	Normalized LC50
Effluent	108	137.3
Lab Water	6.62	6.62

*Normalized LC50 = SWM LC50 x (lab hdns/swm hdns)^0.9422

WER 2-SEPTEMBER 27, 2016

Effluent Hardness (µg/L)	77000
Lab water Hardness (µg/L)	98000
Total Copper SMAV (µg/L)	24
Normalized SMAV	23.5
D. Copper SMAV (µg/L)	22.11
Normalized SMAV	21.7

Total Copper - Ceriodaphnia

	LC50 (µg/L)	Normalized LC50
Effluent	128	160.7
Lab Water	7.25	7.25

*Normalized LC50 = SWM LC50 x (lab hdns/swm hdns)^0.9422

Dissolved Copper - Ceriodaphnia

	LC50 (µg/L)	Normalized LC50
Effluent	105	131.8
Lab Water	6.66	6.66

*Normalized LC50 = SWM LC50 x (lab hdns/swm hdns)^0.9422

FIGURE 1. TOTAL AND DISSOLVED COPPER *CERODAPHNIA DUBIA* LC50'S (RAW AND NORMALIZED) FROM THE JULY AND SEPTEMBER 2016 TOXICITY TESTS.

WER

	Copper	
	Total	Dissolved
WER #1	6.82	6.08
WER #2	7.39	6.93
Geo Mean	7.10	6.49
1/Geo Mean (OWRB)	0.1409	0.1541

Total/Dissolved Translator (f)

	Copper
	(Dissolved/Total)
5/3/2016	0.55
6/27/2016	0.82
6/28/2016	0.69
7/6/2016	0.79
7/7/2016	1.03
7/20/2016	0.85
7/21/2016	0.85
7/26/2016	0.75
7/27/2016	0.75
7/28/2016	0.65
9/27/2016	0.66
Geo Mean	0.75
f	1.33
1/f (OWRB)	0.75

fWER

	Total Copper	Dissolved Copper
WER	7.10	6.49
f	1.33	1.33
fWER (EPA)	9.43	8.62
1/fWER or T (OWRB)	0.106	0.1160

FIGURE 2. TOTAL AND DISSOLVED COPPER WER'S, FWER'S AND DISSOLVED TRANSLATOR (F).