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STUDY PLAN FOR A SITE-SPECIFIC STREAMLINED WATER EFFECT RATIO FOR COPPER

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1. INTRODUCTION AND STUDY OBJECTIVE

The Town of Danville owns and operates the Town of Danville Wastewater Treatment Plant (WWTP) which is a major municipal wastewater treatment plant in Danville, Indiana. Outfall 001 is authorized to discharge to West Fork White Lick Creek via NPDES Permit IN0020079. The Permit was renewed with an effective date of February 1, 2017. In developing the discharge limits for the renewed NPDES Permit, IDEM found that the WWTP effluent levels of total copper had a reasonable potential to exceed (RPE) the in-stream aquatic life criteria. Hence, the renewed Permit contains final water quality-based effluent limits (WQBELs) for total copper with a 3-year compliance schedule. Upon review of the IDEM approach to developing the WQBELs, options to adjust the criteria or the implementation of the criteria to incorporate site-specific (WWTP and West Fork White Lick Creek) conditions were identified.

This work plan identifies the study plan for the development of a site-specific Water Effect Ratio (WER) for copper using the USEPA Streamlined WER Procedure for Discharges of Copper (USEPA, 2001) (Streamlined WER). The potency of toxicants can be highly variable based on in situ water chemistry parameters such as hardness, pH, and total organic carbon content. A WER adjusts state aquatic life standards to reflect the toxicity of a chemical in a site-specific water as compared to its toxicity in the laboratory test water for which the standards are based. For example, a WER is the ratio of the lethal concentration of copper (LC50 value) in site water to the copper LC50 value in laboratory water (or published toxicity data). Per the Streamlined WER procedure, the geometric mean of the two WER determinations is the final site WER (fWER). The site fWER is then applied to the copper criteria (as total) and is used in the calculation of the permit limit using the site-specific receiving water chemistry parameters.

The USEPA water-effect ratio procedure was initially published in 1984 and revised in 1994. The WER Interim Guide (USEPA, 1994) outlines a methodology by which laboratory toxicity tests in site water and laboratory water are conducted with a primary and secondary test species. In 2001, the Streamlined WER procedure was published. The Streamlined WER procedure for copper was developed in response to the need to improve the efficiency of applying the WER approach for the common situation where copper concentrations exceed criteria due to continuous discharges but there is no actual toxicity due to the elevated copper concentrations[1]. “The most common such situation involves municipal effluents, which past experience and current knowledge have generally shown to yield low risks for copper toxicity, due to the sequestering of copper by organic matter” (USEPA 2001). USEPA 2001 goes on to say that “Because this is a relatively common regulatory situation, a great deal of experience is available to guide the development of a more efficient procedure,” and “EPA developed a more streamlined approach, simpler to perform, simpler to review, but fully protective” (USEPA 2001). In short, while still fully protective, the Streamlined WER approach is more efficient, requiring only two sampling events with one test species, utilizing the design low-flow dilution ratio, and allows for the use of the laboratory water test results or the results of a published toxicity database (Species Mean Acute Value or SMAV), whichever is greater, in the calculation of the WER.

The Streamlined WER indicates that the site water used for testing is effluent and upstream receiving water “combined at the dilution corresponding to the design low flow condition that the permitting authority uses in permit limit calculations.” For the West Fork of White Lick Creek, a 7Q10 flow of

[1] The situation described is precisely the case for the Town of Danville. While the data show an RPE for copper, neither acute toxicity (>1.0 TUa) nor chronic toxicity (>1.0 TUc) has been demonstrated in annual WET testing with two organisms (*C. dubia* and *P. promelas*) and 100% effluent.

zero was utilized in the development of the Town of Danville's Permit limits[2]. As such, it is appropriate[3] that the WER determinations be performed using 100% effluent.

The objectives of this Study Plan are as follows:

- Develop a site-specific fWER for total copper following the Streamlined WER approach:
  - Initial rangefinder testing followed by a minimum of two WER determinations with site water (100% effluent) and using one species (*c. dubia*)
  - The site WER though developed with acute testing is applicable to both the acute and chronic critiera[4]
- Collect effluent samples over a period of 3 to 5 months in order to assess and capture possible variability.
- Generate valid and representative data by including QA/QC and data handling elements in the plan.

[2] For example, application is observed in not only in the final copper limitations, but also in the WET limitations (benchmark of 1.0 TUc).

[3] By deferring to the design low flow conditions in permit limit calculations, the Streamlined WER recognizes that the appropriate "critical" condition for protection can vary and will already be identified by the permitting authority. It is not uncommon for the "critical" condition to be no dilution (100% effluent, with compliance for both acute and chronic criteria applied at the end-of-pipe) and the Streamlined WER document does not include a prohibition on the range of dilution (including no dilution) allowed. Further supporting the appropriateness of using the Streamlined WER with 100% effluent (for 7Q10=0 receiving waters) are comments made by EPA Region 6 (AR0040967, 2014) on a draft plan proposed by an Arkansas NPDES facility. In the comments, the EPA instructed the facility that for the Streamlined WER procedure (for copper), they are to use 100% effluent: "…under the copper streamlined procedure, the simulated downstream water constitutes effluent and upstream water mixed at the design low flow dilution ratio (in the case of Van Buren's discharge, this means 100% effluent)."

[4] Both the Streamlined WER procedure (2001) and the October 2000 document "Response to Peer Review Comments on Streamlined Water-Effect Ratio Procedure for Discharges of Copper" (Delos et. al, 2000) confirm the appropriateness of this approach. From the Streamlined WER procedure: "In accord with the 1994 Interim Guidance and with common practice, the WER derived from acute tests is applied to both acute and chronic criteria. Because the involvement of strong binding agents causes the WER to increase as the effect concentration decreases, the WER derived from acute tests is expected to be protective of chronic effects." From Delos et. al, 2000 (in question and response form): "It was unclear if the WER derived from the streamlined procedure would apply only to acute criteria. Since this WER is essentially derived from acute data, wouldn't it potentially underestimate toxicity at a chronic level? The document has been clarified to indicate that the acute WER does apply to chronic criteria, per conventional practice. Although the chronic criterion is less than the acute criterion, this does not mean that the chronic WER is less than the acute WER. Rather the opposite is true. Because strong binders with limited capacity are involved, the "water-effect difference" (as opposed to ratio) tends to be similar across various effect concentrations. As a result the ratio tends to increase the sensitive the endpoint considered." (note that it is believed this last sentence includes a typo and that the phrase "sensitive the endpoint" was meant to read "sensitivity of the endpoint")

2. SAMPLING PLAN

2.1 Sampling Frequency and Plan

The Streamlined WER method requires a minimum of two WER determinations, approximately 30 days apart. Prior to the WER tests, an initial rangefinder test will be performed in order to properly target the appropriate test concentrations for use in the WER determinations.

Sampling events will occur from approximately August 2017 – October 2017 with Outfall 001 sample collection once per 30 days. Sample collection will overlap with routine Outfall 001 NPDES required monitoring for total copper, total lead, CBOD5, TSS, Ammonia-N, and pH.

2.2 Sampling Location

Effluent samples will be collected from the existing Outfall 001 monitoring location.

2.3 Sample Types and Collection

All samples for the rangefinder testing and WER determinations will be 24-hr composites. Samples for concurrent NPDES analytes will be as required by the NPDES Permit.

3. ANALYTICAL METHODS

Per the Streamlined WER procedure, analysis of select chemical parameters from the initial site water (in this case 100% effluent) and from reconstituted test water (laboratory control water) is required. This section is applicable only to these samples and not the concurrent NPDES monitoring. Table 1 provides an overview of the chemical testing associated with the WER determination testing.

Critical analyses recommended by the Streamlined WER method will be conducted by TestAmerica. EPA Method 200.8 will be used for analysis of total copper, Standard Method 5310 for dissolved organic carbon (DOC) and EPA 160.2 for total suspended solids (TSS). Anticipated method detection limits (MDL) and reporting limits (RL) without sample dilution are as follows:

- Copper MDL = 1.2 µg/L
- Copper RL = 2.0 µg/L
- DOC MDL = 0.5 mg/L
- DOC RL = 1.0 mg/L
- TSS MDL = 0.7 mg/L
- TSS RL = 1.0 mg/L

No extra QA/QC will be requested in association with the above analyses. TestAmerica will follow applicable method specific QA/QC requirements. Supporting documentation regarding qualifications for TestAmerica is available upon request.

Ramboll Environ will be responsible for documenting supporting water quality laboratory analysis, consistent with USEPA 2002. Ramboll Environ maintains written Standard Operating Procedures (SOPs) adhering to USEPA (2002) methodologies for *C. dubia* (SOPs available upon request).

Table 1. WER Determination Chemical Analysis

Parameter	Method	Test Schedule
Total Copper	EPA 200.8	test initiation; test termination
DOC	SM 5310	test initiation before copper addition
TSS	EPA 160.2	test initiation before copper addition
Total Residual Chlorine	SM 4500-Cl G	test initiation before copper addition
Total Ammonia	SM 4500-NH3 D	test initiation before copper addition
Total Hardness	SM 2340 C	test initiation before copper addition
Total Alkalinity	SM 2320 B	test initiation before copper addition
pH	SM 4500-H+ B	test initiation; after 24 hrs; test termination
Dissolved Oxygen	SM 4500-OG	test initiation; after 24 hrs; test termination
Specific Conductance	SM 2510 B	test initiation; after 24 hrs; test termination
Temperature	SM 2550 B	test initiation; after 24 hrs; test termination

4. TOXICITY TESTING

Ramboll Environ will perform the Streamlined WER determinations in their Nashville, TN Ecotoxicology Laboratory. The steps to perform the WER testing are outlined below. In addition, Table 2 provides a simplified overview of the key components and test conditions.

Table 2. Overview of Streamlined WER Determination*

Summary of Test Conditions for a *C. dubia* Acute WER Determination	
Type Testing	48-hr Acute
Test Species	*Ceriodaphnia dubia (C. dubia)*
Organism Age	< 24 hrs old at test initiation
Number of Test Concentrations	Minimum of five plus a control
Number of Replicates	Four
Number of Organisms per Replicate	Five
Feeding During Test	None
Temperature	25±1°C
Photoperiod	Light:Dark 16h:8h
Copper source	Concentrated stock solution of reagent grade copper sulfate (will not dilute waters by more than 10%)
Endpoint	Mortality
*Side-by-Side testing will be conducted with Site Water (100% effluent) and with Lab Control Water (with similar hardness to the Site Water).	

- USEPA Streamlined WER Procedure for Discharges of Copper (USEPA, 2001) will be followed. The method requires a minimum of two WER determinations, approximately one month apart. Prior to the WER tests, an initial rangefinder test will be performed in order to properly target the appropriate test concentrations.
- Site water will consist of undiluted Outfall 001 effluent. The laboratory test waters will be reconstituted waters prepared according to USEPA (2002).
  - Site water is to be collected during normal operating conditions
  - Site water will be filtered, if necessary, through a plankton net to remove any indigenous organisms prior to toxicity testing.
- Tests will be initiated as soon as possible after sample collection but always w/in 96 hours of collection as indicated in Appendix A, Section C.8 of the USEPA Streamlined WER Procedure.
- The test temperature will be 25 +/- 1 ^{o}C with a light:dark photoperiod of 16h:8h.
- The test compound used for spiking will be reagent-grade copper sulfate. This will facilitate comparison of toxicity test results to those published in the USEPA ambient water quality criteria document for copper (USEPA, 2007) when evaluating WER test species sensitivity versus that demonstrated in previously published studies by USEPA's Streamlined WER for Copper.
  - Copper sulfate will be added to distilled water to prepare the stock solution for addition to test waters. The stock solution will be of sufficient copper concentration that its addition to test waters (i.e., laboratory water or site water) will not dilute the test water by greater than 10%. Given the high solubility of copper sulfate, stirring of test solutions will be for a minimum of 15 minutes. In keeping with Appendix A, Section E.15 of the USEPA Streamlined WER Procedure, the mixture will be allowed to stand for 2 to 24 hours prior to use. If standing occurs overnight, the sample will be kept at < 4 °C.
- The test species will be *C. dubia* and will be obtained from in-house cultures[5].

[5] Acute *C. dubia* in-house reference toxicity test results, for assessment of organism health, are available upon request.

- Acute, 48 hour toxicity tests will be conducted following USEPA (2002) methodologies. Mortality (lack of movement upon gentle prodding) will be the test endpoint[6].
  - Ramboll Environ maintains written Standard Operating Procedures (SOPs) adhering to USEPA (2002) methodologies for *C. dubia* (SOPs available upon request).
- *C. dubia* neonates will be less than 24 hours old at test initiation per USEPA (2002). Test organisms will not be fed during the test.
- Borosilicate glass beakers will be utilized as the test vessels. Four replicates of five organisms per vessel will be established. Test solution volumes (copper and control exposures) will be a minimum of 15 mL (USEPA, 2002). Test vessels will be covered with clear plastic sheet during testing in such a manner as to allow light penetration and gas exchange.
- Following initial range-finding tests of copper in site water and laboratory water, the WER test series for test waters will be determined. The toxicity test dilution series will utilize a dilution factor of 0.7.
- Definitive (minimum of five copper exposures), static non-renewal toxicity tests will be conducted.
- The test water will be the effluent and reconstituted water for determinations of the laboratory water LC50 values.
  - The laboratory test waters will be reconstituted water (total hardness similar to that of the effluent, since the 7Q10 of the receiving stream is zero, no upstream receiving water will be used in the tests).
- A “laboratory control” of moderately hard water will be established in parallel with each site water test to confirm the suitability of test organisms in the event of toxicity in the site water control.
- Ramboll Environ will document water quality parameters in test waters and test exposures as follows using standard methods:
  - At test initiation in test waters (effluent and reconstituted waters) prior to copper addition:
    - total residual chlorine, total ammonia, total hardness, total alkalinity, pH, dissolved oxygen, specific conductance, DOC, TSS and temperature.
  - At test initiation, after 24 hours, and at test termination in control and all copper exposures:
    - pH, dissolved oxygen, specific conductance, and temperature.
- Total Copper analyses will be conducted at test initiation and termination in all control and copper exposures. The average of these concentrations will be used in all calculations.
  - Samples for total copper analysis will be collected by Ramboll Environ upon test solution preparation and at test termination. Aliquots of the samples will be immediately collected in appropriate sample vessels with preservative. These aliquots will be sent to a local contract laboratory for total copper analysis[7]. Copper analysis will be by USEPA Method 200.8 (reporting limits and method detection limits are presented in Section 3.0).
- The control water *C. dubia* copper LC50 values will be compared to *C. dubia* copper LC50 values published by USEPA (2007) in similar hardness waters to confirm that the sensitivity of Ramboll Environ test organisms is similar to that listed in the USEPA criteria database.
- All LC50 values will be determined based on the average measured copper concentration in test solutions. LC50 values will be determined using commercial software approved by USEPA (CETIS, version 1.8.4.22). Toxicity determinations will be made only for tests meeting test acceptability criteria (i.e., 10 percent mortality or less in the primary dilution water control). Should the difference between the two tests be greater than five (5), an additional WER test will be conducted.

[6] The Streamlined WER Procedure for Discharges of Copper requires acute testing only, as acute test results have been shown to be protective of chronic effects.
[7] TestAmerica Laboratories, Inc. TestAmerica Nashville, 2960 Foster Creighton Drive, Nashville, TN 37204

- The final site WER (fWER) will be determined as the geometric mean of the *C. dubia* WER values, for the two or three determinations. A value of five (5) will be used (in calculation of the fWER) for any WER values greater than five (5) so that the fWER will be five (5) or less..
- Study results will be reported according to USEPA (2001).

5. DATA HANDLING

All data will be evaluated with respect to the required laboratory QA/QC requirements. In addition, the following specific approaches will be utilized.

- Chemical data will be reported to the MDL.
- The MDL will be substituted as the result value for non-detect results at the MDL.
- Estimated results between the MDL and RL will be used as reported.
- For total copper data, the average of test initiation and test termination concentrations will be used in calculations of the WER.
- Toxicity test data will be reported as a Lethal Concentration to 50% of the exposed organisms (LC50).
- The final site WER (fWER) will be determined by taking the geometric mean of the two or three WER determinations. A value of five (5) will be used (in the calculation of the fWER) for any WER values greater than five (5) so that the fWER will be five (5) or less.
- Reference toxicity test data will be supplied upon request.

6. REFERENCES

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