



Re-Evaluation of Copper Impact from Wilkeson Wastewater Treatment Plant on Wilkeson Creek

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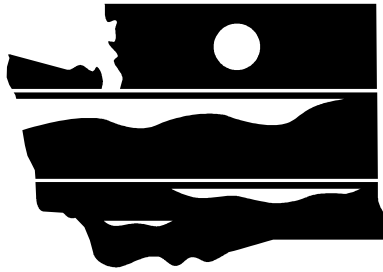
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E C O L O G Y

Re-Evaluation of Copper Impact from Wilkeson Wastewater Treatment Plant on Wilkeson Creek

by
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Environmental Assessment Program
Olympia, Washington 98504-7710

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Abstract

Wilkeson Creek, a tributary to the Carbon River in Pierce County, is on the 1998 303(d) list for exceeding state aquatic life standards for copper. The listing is based on a copper concentration of 37 µg/L measured in a composite effluent sample from Wilkeson Wastewater Treatment Plant (WWTP), collected in November 1995.

This re-evaluation is a more intensive study of copper in the WWTP effluent and receiving water. Eight sampling events from July through November 2000 provided data on copper concentrations, general water quality chemistry, and flow for the WWTP effluent and for Wilkeson Creek above and below the outfall.

Copper concentrations upstream and downstream of the WWTP outfall were well within water quality standards during each of the eight sampling events. The maximum dissolved copper concentration found downstream of the outfall was 0.78 µg/L. The maximum total recoverable copper concentration found in the WWTP effluent was 36.4 µg/L. An analysis with a water quality standards spreadsheet developed by Ecology's Water Quality Program, TSDCALC 9, showed there was no reasonable potential for copper concentrations to exceed water quality standards for critical low-flow conditions or for any of the sampling event conditions.

Based on the findings of this study, it is recommended that Wilkeson Creek (WA-10-1087, ID # NX07HW, Township 19N, Range 06E, Section 28) be removed from the 303(d) list for copper, and that no limit for copper be included in the Wilkeson Creek WWTP permit.

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 - ◇ Morgan Roose for data reduction and entry of the project to EIM.

Introduction

Wilkeson Creek, a tributary to the Carbon River in Pierce County (Figure 1), is on the 1998 303(d) list¹ for exceeding state aquatic life standards for copper. The listing is based on a total recoverable copper concentration of 37 µg/L (parts per billion) measured in a composite effluent sample from Wilkeson Wastewater Treatment Plant (WWTP), collected by the Washington State Department of Ecology (Ecology) in November 1995. This concentration was calculated to exceed the acute standard at the edge of the dilution zone by a factor of 1.8 (Hoyle-Dodson, 1997). However, since instream flows were not measured at the time of sampling, it could not be determined if the water quality standard was actually violated.

The town of Wilkeson replaced an existing aerated lagoon system, upgrading in 1999 to a secondary activated-sludge treatment plant with UV disinfection. The Ecology Southwest Regional Office (SWRO) requested a study to determine if the new facility had reduced copper sufficiently or if further actions are needed to protect water quality. SWRO specified that the study include sampling Wilkeson Creek and measuring flow, neither of which were done in the previous effort.

In response to this request, Ecology's Environmental Assessment Program monitored copper concentrations in Wilkeson WWTP effluent and in Wilkeson Creek. Ancillary variables included flow, temperature, pH, conductivity, total suspended solids, and hardness. The objectives were to:

- 1) Obtain accurate data on total recoverable copper in Wilkeson WWTP effluent
- 2) Obtain accurate data on dissolved and total recoverable copper in Wilkeson Creek above and below the WWTP
- 3) Evaluate the WWTP's impact on copper concentrations in Wilkeson Creek and the appropriateness of the 303(d) listing
- 4) Obtain sufficient data so that a permit limit for total recoverable copper could be calculated by SWRO if needed

Sampling was conducted on eight occasions, approximately every two weeks from late July through November 2000. EPA (1996) recommends a minimum of eight samples for studies designed to calculate effluent limits for metals. The sampling period was selected by SWRO to represent a broad range of flow conditions and to include the months monitored in the earlier Ecology study (Hoyle-Dodson, 1997).

¹ WA-10-1087, ID # NX07HW, Township 19N, Range 06E, Section 28

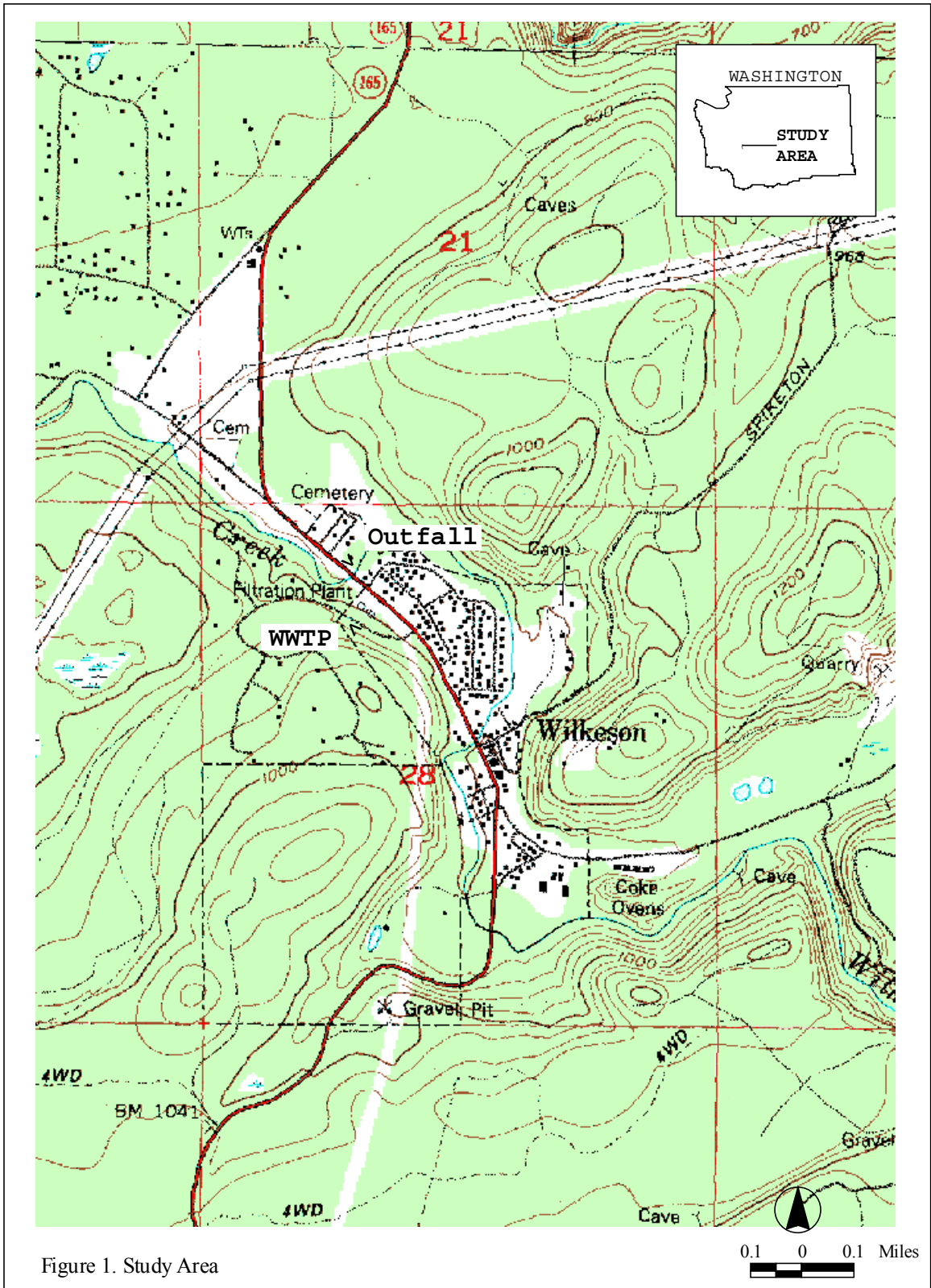


Figure 1. Study Area

Methods

Clean sampling techniques were used following the guidance in EPA Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Levels* (EPA, 1995).

Samples for the study were collected at the sites shown in Table 1.

Table 1 – Sampling Site Locations

| Station | Latitude | Longitude |
|---------------------|---------------|----------------|
| WWTP outfall | N 47° 06' 47" | W 122° 03' 15" |
| creek above outfall | N 47° 06' 50" | W 122° 03' 17" |
| creek below outfall | N 47° 06' 36" | W 122° 03' 08" |

All samples were simple grabs. WWTP samples were collected from a mixing box downstream of the final clarifier. The location of each sampling site was determined with a handheld Magellan GPS Model 320 receiver. The above-plant samples were collected midstream approximately 200 feet upstream of the outfall, at a site representative of creek water prior to mixing with the WWTP effluent. The below-plant sample location was selected during the initial sampling event July 26, 2000. Dye was added to the WWTP effluent, and a sampling location was selected approximately 500 feet downstream of the outfall. It was at this location, just downstream of some small rapids, that the dye appeared to be evenly distributed across the width of the creek. The even dispersion of the dye indicated the complete mixing of effluent with creek water at this sampling location.

Copper samples were collected directly into pre-cleaned 0.5 liter Teflon bottles. The effluent samples were taken with the teflon bottle attached to a plastic pole. The creek samples were taken away from the bank by wading into the channel. Samples for ancillary water quality parameters were collected in appropriate sample containers obtained from the Ecology Manchester Environmental Laboratory.

Samples for dissolved copper were filtered in the field through pre-cleaned 0.45 µm Nalgene filter units (#450-0045, type S). The filtrate was transferred to a new pre-cleaned 0.5 liter Teflon bottle. The total recoverable and dissolved samples were preserved to pH <2 with sub-boiled 1:1 nitric acid, carried in small Teflon vials, one per sample. Teflon sample bottles, Nalgene filters, and Teflon acid vials were obtained from Manchester Laboratory, cleaned as described in Kammin, et al. (1995), and sealed in plastic bags. Powder-free nitrile gloves were worn by personnel sampling and filtering the samples. Filtering was done in a glove box constructed of a PVC frame and polyethylene cover.

Flows were measured with a Swoffer or Marsh-McBirney meter and top-setting rod. pH was measured with an Orion model 250A. Temperature was measured with an electronic thermocouple-type thermometer.

The samples were placed in polyethylene bags and held on ice for transport to Ecology HQ. The copper and hardness samples were stored at 4°C at Ecology headquarters and analyzed as one sample set at the end of the study, within the holding time of six months. The general chemistry samples were transported to Manchester Laboratory within one day of collection. Chain-of-custody was maintained.

Appendix A shows the sampling schedule for the project.

Total recoverable copper was analyzed in the effluent samples. By regulation, permit limits must be expressed as total recoverable metals. Both dissolved and total recoverable copper were analyzed in the upstream and downstream samples to determine concentrations of copper in the creek and to provide data to calculate the fraction of total recoverable copper that is in the dissolved form. This fraction is the metals translator needed to calculate permit limits (EPA, 1996). Analysis of the upstream samples established the background level of dissolved copper.

Analytical Methods

Copper was analyzed at Manchester Laboratory by ICP-MS, following EPA Method 200.8. Total recoverable samples were digested with a mixture of nitric acid and hydrochloric acid in Teflon beakers in a class 100 clean hood. Hardness, conductivity, and total suspended solids were analyzed by Standard Methods 2340B, EPA Method 120.1, and EPA Method 160.2, respectively.

Quality Control Procedures

Field quality control (QC) samples included filter blanks, bottle blanks, and field replicates, at the frequency indicated in Appendix A.

Because of the importance of establishing blank contributions to the copper concentrations measured in the field samples, two sets of filter and bottle blanks were prepared. The method blank was analyzed in duplicate to provide an estimate of variability in the blank response.

Field replicates (samples collected separately approximately five minutes apart) and duplicate laboratory analyses of the replicates were used to obtain an estimate of the total standard deviation from sampling and analysis. The field replicates consisted of three downstream sample pairs each for dissolved and total recoverable copper, and three effluent sample pairs for total recoverable copper. One sample from each of these replicate pairs was analyzed in duplicate (split at the laboratory). These samples were collected on three separate dates.

Laboratory QC samples for copper included a standard reference material (SLRS-3 or equivalent), laboratory control sample, method blank, duplicate analyses, matrix spikes, and matrix spike duplicates, as indicated in Appendix A. The SRM, LCS, and method blank were analyzed in duplicate.

Data Quality

Data for this project met all quality assurance (QA) and QC criteria and can be used without qualification except as noted below. Matrix spike recovery ranged from 108 to 110%, well within relevant control limits. Precision estimates based on duplicate spike analyses were all within the acceptance criteria of +/- 20%.

The standard reference material was SLRS-4 (St. Lawrence River Water) with a certified value of 1.81 µg/L. Reference material analyses ranged from 102 to 117% of the certified value.

Method blanks for both total recoverable and dissolved copper had no detectable copper at a practical quantitation limit of 0.1 µg/L.

The average relative percent difference (RPD) between field replicates was 15% for total recoverable copper and 1.2% for dissolved copper in the receiving water (Table 2). The RPD between field replicates of WWTP effluent was 4.7% for total recoverable copper. RPD is calculated by dividing the difference in sample results by the mean of the results, the fraction expressed as a percentage.

The standard deviations for sampling were 1.56 µg/L for total recoverable copper and 0.3×10^{-5} µg/L dissolved copper below the outfall, and 0.11 µg/L total recoverable copper in the effluent.

The standard deviations for sampling (field replicates) and analysis (laboratory duplicates) are shown in Table 2.

Table 2 – Standard Deviations of Field Replicates and Laboratory Duplicates (µg/L)

| | Sampling Std. Dev.s (Field Replicates) | Laboratory Std. Dev.s (Laboratory Duplicates) |
|----------------------------|---|--|
| Below, Total Recov. Copper | 0.11 | 0.08 |
| Below, Dissolved Copper | <0.01 | <0.01 |
| WWTP, Total Recov. Copper | 1.56 | 2.16 |

Table 3 shows there was little difference between total variability (from sampling and analysis as represented by field replicates) and analysis variability (from laboratory duplicates). This suggests that the variability was in large part due to variability in laboratory analysis.

Total recoverable copper for sample 438034, 16.9 µg/L (below outfall – 10/24/00) was rejected as an outlier because (1) the value was an order of magnitude higher than the values for the creek below the outfall on other dates and (2) the value could not be reconciled with a mass balance of copper concentrations upstream and in the WWTP effluent found on 10/24/00.

Total recoverable copper in field replicate sample 308031 was qualified as an estimated value because of a high RPD between laboratory duplicates. Complete laboratory QA reports appear in Appendix B.

All filter blanks and bottle blanks showed no detected copper at a detection limit of 0.1 µg/L.

Table 3 -Wilkeson Creek Field Quality Control Sample Results

| Wilkeson Creek Below WWTP | | | | | |
|---------------------------------|--------|-----------|-----------------------|-----------|-----------|
| Total Recoverable Copper | | | | | |
| | (ug/L) | | | Sample | Replicate |
| Date | Sample | Replicate | RPD | Lab Log # | Lab Log # |
| 7-26-00 | 1.17 | 0.99 | 17% | 308032 | 308031 |
| 9-07-00 | 0.83 | 0.78 | 6% | 368064 | 368067 |
| 11-28-00 | 0.86 | 0.69 | 22% | 488035 | 488036 |
| | | | 15% = Avg RPD | | |
| Dissolved Copper | | | | | |
| | (ug/L) | | | Sample | Replicate |
| | Sample | Replicate | RPD | Lab Log # | Lab Log # |
| | 0.57 | 0.58 | 1.7% | 308032 | 308031 |
| | 0.63 | 0.63 | 0.0% | 368064 | 308067 |
| | 0.51 | 0.50 | 2.0% | 488035 | 488036 |
| | | | 1.2% = Avg RPD | | |
| WWTP Effluent | | | | | |
| Total Recoverable Copper | | | | | |
| | (ug/L) | | | Sample | Replicate |
| Date | Sample | Replicate | RPD | Lab Log # | Lab Log # |
| 7-26-00 | 33.0 | 36.4 | 9.8% | 308037 | 308036 |
| 9-07-00 | 33.8 | 33.0 | 2.4% | 368065 | 368068 |
| 11-28-00 | 16.2 | 16.5 | 1.8% | 488033 | 488034 |
| | | | 4.7% = Avg RPD | | |
| Field Blanks* | | | | | |
| | (ug/L) | (ug/L) | | Sample | Replicate |
| Date | Filter | Bottle | | Lab Log # | Lab Log # |
| | Blank | Blank | | | |
| 7-26-00 | 0.1 U | 0.1 U | | 308034 | 308035 |
| 11-28-00 | 0.1 U | 0.1 U | | 488032 | 488031 |

* - The filter blank is a dissolved copper field blank. The bottle blank is a total recoverable copper field blank.

RPD - Relative percent difference

U - The analyte was not detected at or above the reported result.

Results

Comparison of Wilkeson Creek Samples to Water Quality Standards

Results from the eight days of sampling are summarized in Table 4. The average and maximum background levels of dissolved copper in Wilkeson Creek upstream of the WWTP outfall were 0.50 and 0.66 µg/L, respectively. The average and maximum dissolved copper concentrations downstream of the WWTP were 0.59 and 0.78 µg/L, respectively. The average dissolved and total recoverable copper concentrations in the creek during the study period were both significantly higher downstream of the outfall (paired t-test, $p < 0.05$). All concentrations in the creek were well below the acute and chronic state freshwater quality standards of 5.28 and 3.93 µg/L, respectively, for the critical case of a hardness of 28.9 mg/L, the lowest measured for any sampling date.

Dilution Factor Determination

The dilution factors at the edges of the acute and chronic mixing zones for the WWTP outfall were estimated with RIVPLUM 5, which models a point source in a river with boundary effects from the shoreline (<http://www.ecy.wa.gov/programs/eap/pwspread/pwspread.xls>). Based on the RIVPLUM analysis, the dilution factors were 108 chronic, and 37 acute. The Ecology Water Quality Program Permit Writer's Manual (1994) requires that the mixing zone be limited to 25% of creek width for the chronic dilution factor and 2.5% for the acute dilution factor, based on 7Q10 flow. The lowest stream flow during the study period, 5.37 cfs on August 24, 2000, was used to represent 7Q10 conditions because no historic flow data are available for Wilkeson Creek. Based on the WWTP flow for the same date, chronic and acute dilution factors of 39.3 and 4.83, respectively, were calculated. These dilution factors apply because they are more restrictive than those calculated by RIVPLUM.

Reasonable Potential Determination

The Ecology Water Quality Program TSDCALC 9 spreadsheet was used to make a determination of whether there is a reasonable potential for water quality standards for copper to be exceeded at the edge of the chronic and acute mixing zones (Appendix C – <http://ecy.wa.gov/programs/eap/pwspread/tsdcalc9.xlw>).

TSDCALC 9 found no reasonable potential for copper water quality violations for any of the sampling events. A low-flow condition was found on August 24, the date for which the dissolved copper concentrations at the edge of the mixing zones were closest to the standards. The maximum dissolved copper concentrations at the edges of the chronic and acute mixing zones were calculated to be 1.70 and 10.15 µg/L, respectively, for August 24. The freshwater standards for copper were 8.55 and 12.45 µg/L, respectively, based on a receiving water hardness of 71.8 mg/L for this date.

Table 4 - Wilkeson Creek and Wilkeson WWTP Results

| Date: | | 7-26-00 | 8-24-00 | 9-07-00 | 9-19-00 | 10-12-00 | 10-24-00 | 11-14-00 | 11-28-00 |
|----------------|---------------------|---------|---------|---------|---------|----------|----------|----------|----------|
| Time: | | 1045 | 1205 | 1120 | 1050 | 1110 | 1305 | 1120 | 1120 |
| Lab Sample #:* | | 308038 | 348003 | 368063 | 388053 | 418023 | 438033 | 468043 | 488030 |
| RIVER | TR Cu (ug/L) | 0.71 | 0.69 | 0.82 | 0.73 | 0.73 | 0.63 | 0.57 | 0.81 |
| UPSTREAM OF | Dissolved Cu (ug/L) | 0.40 | 0.50 | 0.49 | 0.66 | 0.55 | 0.47 | 0.45 | 0.47 |
| WWTP | Hardness (mg/L) | 57.1 | 73.0 | 66.0 | 61.3 | 51.8 | 32.6 | 37.1 | 28.9 |
| OUTFALL | TSS (mg/L) | 1 | 1 | <1 | <1 | <1 | <1 | <1 | 7 |
| LAB RESULTS | Cond. (umhos/cm) | 140 | 174 | 151 | 131 | 117 | 82.5 | 85.5 | 66 |
| FIELD RESULTS | Flow (cfs) | 12.32 | 5.37 | 10.4 | 12.53 | 15.9 | 32.14 | 30.95 | 77.95 |
| | Temp (degrees C) | 13.3 | 14.0 | 12.8 | 13.8 | 9.2 | 7.3 | 3.3 | 3.7 |
| | pH up | 7.8 | 7.8 | 8.2 | 8.2 | 7.3 | 7.5 | 7.8 | -- |

| Date: | | 7-26-00 | 8-24-00 | 9-07-00 | 9-19-00 | 10-12-00 | 10-24-00 | 11-14-00 | 11-28-00 |
|----------------|---------------------|---------|---------|---------|---------|----------|----------|----------|----------|
| Time: | | 1330 | 1300 | 1200 | 1145 | 1145 | 1250 | 1155 | 1150 |
| Lab Sample #:* | | 308031 | 348004 | 368064 | 388054 | 418024 | 438034 | 468044 | 488035 |
| RIVER | TR Cu (ug/L) | 1.17 | 1.48 | 0.83 | 1.07 | 0.74 | REJ | 0.88 | 0.86 |
| DOWNSTREAM | Dissolved Cu (ug/L) | 0.57 | 0.78 | 0.63 | 0.68 | 0.62 | 0.48 | 0.46 | 0.51 |
| OF WWTP | Hardness (mg/L) | 56.0 | 71.8 | 66.3 | 63.4 | 52.4 | 33.0 | 37.8 | 29.2 |
| OUTFALL | TSS (mg/L) | 1 | <1 | 2 | 1 | <1 | 1 | 1 | 4 |
| LAB RESULTS | Cond. (umhos/cm) | 141 | 178 | 152 | 132 | 118 | 83.1 | 95.3 | 66.7 |
| FIELD RESULTS | Temp (degrees C) | 14.3 | 14.3 | 12.2 | 13.9 | 9.3 | 7.3 | 3.4 | 3.7 |
| | pH | 7.9 | 7.8 | -- | -- | -- | 7.1 | -- | -- |

| Date: | | 7-26-00 | 8-24-00 | 9-07-00 | 9-19-00 | 10-12-00 | 10-24-00 | 11-14-00 | 11-28-00 |
|---------------|------------------|---------|---------|---------|---------|----------|----------|----------|----------|
| Time: | | 1010 | 1340 | 1225 | 1245 | 1245 | 1105 | 1255 | 1100 |
| Lab Sample #: | | 308037 | 348005 | 368065 | 388055 | 418025 | 438035 | 468045 | 488033 |
| WWTP | TR Cu (ug/L) | 33.0 | 36.4 | 33.8 | 35.5 | 34.2 | 27.1 | 22.5 | 16.2 |
| LAB RESULTS | Hardness (mg/L) | 117 | 112 | 122 | 120 | 120 | 106 | 118 | 111 |
| | TSS (mg/L) | 12 | 11 | 9 | 9 | 8 | 10 | 8 | 8 |
| | Cond. (umhos/cm) | 591 | 588 | 607 | 610 | 567 | 516 | 490 | 439 |
| FIELD RESULTS | 24-hr flow (cfs) | 0.0166 | 0.0353 | 0.0309 | 0.0309 | 0.0294 | 0.0309 | 0.0309 | 0.0387 |
| | Temp (degrees C) | 16.9 | 19.3 | 15.5 | 18.2 | 12.3 | 9.6 | -- | 7.9 |
| | pH | 7.5 | 7.3 | 6.8 | 7.4 | -- | 7.6 | 7.1 | -- |

* Lab Sample #s refer to copper samples.

Cu - copper

REJ - The data are unusable for all purposes

TR - total recoverable

Cond - conductivity

The TSDCALC 9 determinations were made with spreadsheet default values of 0.996 for the ratio between dissolved and total copper. A site-specific copper translator was calculated to be 0.95, based on the 95th percentile of the natural log distribution of the translators from each of the eight sampling dates, in accordance with EPA guidance (EPA, 1996). The Ecology document *Application of Metals Standards* (Ecology, 1996) suggests the use of a minimum of 20 data points of overall flow (versus critical low flow) data to determine a site-specific metals translator. For this reason, the TSDCALC 9 default translator of 0.996 was used, rather than the less conservative 0.95 site-specific translator.

Other inputs to TSDCALC 9 included maximum effluent concentration of 36.4 µg/L, n=8, and a coefficient of variation of 0.14, based on the eight effluent total recoverable copper concentration data points.

Comparison of Re-Evaluation with Initial Assessment

The original assessment of the reasonable potential for a violation of water quality standards for copper found a reasonable potential for violation (Hoyle-Dodson, 1997). That assessment was based on one data point representing effluent copper concentration (n=1 in TSDCALC 9). When a single data point is applied to TSDCALC 9, the results are considerably conservative, favoring the finding of the possibility of a reasonable potential.

This re-evaluation was based on eight effluent data points (n=8). In addition, seasonal copper concentrations, creek flow, and hardness concentrations were used in the evaluation, which was not done in the original assessment. With this improved data set, it was found that there is no reasonable potential for a violation of state water quality standards for copper in Wilkeson Creek in the vicinity of the Wilkeson Creek WWTP outfall.

Recommendations

Based on the finding of no violations of water quality standards for acute or chronic copper concentrations in Wilkeson Creek and no reasonable potential for violations at the edge of the acute or chronic mixing zone, it is recommended that the water segment (WA-10-1087, ID # NX07HW, Township 19N, Range 06E, Section 28) be removed from the 303(d) list for copper and that no limits for copper be included in the Wilkeson WWTP NPDES permit.

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Appendices

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| Appendix A - Sampling Schedule | | | | | | |
|---------------------------------------|---------------------------------------|------------------------|---------------------|---------------------|-----------------|---------------|
| | | | | | | |
| Sample Type | Analysis | # of Samples per Event | | | Sampling Events | Total Samples |
| | | WWTP | Creek Above Outfall | Creek Below Outfall | | |
| Field Samples | Dissolved Cu | | 1 | 1 | 8 | 16 |
| " | Total Recov. Cu | 1 | 1 | 1 | 8 | 24 |
| " | Hardness | 1 | 1 | 1 | 8 | 24 |
| " | TSS | 1 | 1 | 1 | 8 | 24 |
| " | Conductivity | 1 | 1 | 1 | 8 | 24 |
| " | Dissolved Cu | | | 1 | 3 | 3 |
| " | Total Recov. Cu | 1 | | 1 | 3 | 6 |
| Lab Duplicates | Dissolved Cu | | | 1 | 2 | 2 |
| " | Total Recov. Cu | 1 | | 1 | 2 | 4 |
| Filter Blanks | Dissolved Cu | | | | 2 | 2 |
| Bottle Blanks | Dissolved Cu | | | | 2 | 2 |
| Dup. Matrix Spikes | Dissolved Cu | | 2 | | 1 | 2 |
| " | Total Recov. Cu | 2 | 2 | | 1 | 4 |
| Std. Ref. Material | Cu | | | | 1 | 2 |
| Lab Control Sample | Cu | | | | 1 | 2 |
| Method Blank* | Dissolved Cu | | | | 1 | 1 |
| " | Total Recov. Cu | | | | 1 | 1 |
| | | | | | | |
| | * Method Blanks analyzed in duplicate | | | | | |
| | | | | | | |

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Appendix B - Laboratory Quality Assurance

General Chemistry

SUMMARY

The data generated by the analysis of these samples can be used without qualification.

SAMPLE INFORMATION

Samples were received in good condition.

HOLDING TIMES

All analyses were performed within established EPA holding times

ANALYSIS PERFORMANCE

Instrument Calibration

Instrument Calibration was checked by initial calibration verification standards and blanks. All initial and continuing calibration verification standards were within control limits. A correlation coefficient of 0.995 or greater was met. Balances are professionally calibrated yearly and calibrated in-house daily. Oven temperature is recorded before and after each analysis batch.

Procedural Blanks

The procedural blanks associated with these samples showed no significant analytical levels of analytes.

Spiked Sample Analysis

Spiked sample analyses were performed where applicable with all spike recoveries within acceptance limits of 25%. Spiked sample analysis is performed at a frequency of at least 5%.

Precision Data

Spiked sample results and duplicate sample results were used to evaluate precision on this sample set. Relative Percent Difference (RPD) for general chemistry parameters were within acceptance limits of +/- 20% for duplicate analysis. Laboratory duplication is performed at a frequency of at least 10%. Precision and accuracy specifications are

based on sample concentrations greater than four times the reporting limit. For results near the reporting limit, the criteria are not guaranteed to be better than +/- the method detection limit.

Laboratory Control Sample (LCS) Analyses

LCS analyses were within the windows established for each parameter.

Metals

SUMMARY

Data for this project met all QA and QC criteria and can be used without qualification.

SAMPLE RECEIPT

The samples were received by the Manchester Laboratory on 11/29/00 in good condition.

HOLDING TIMES

All analyses were performed within the specified holding times (180 days).

INSTRUMENT CALIBRATION

Instrument calibration was performed before each analytical run and checked by initial calibration verification standards and blanks. Continuing calibration standards and blanks were analyzed at a frequency of 10% during the run and again at the end of the run. All initial and continuing calibration verification standards and blanks were within the relevant control limits (90-110%).

PROCEDURAL BLANKS

The procedural blanks associated with this sample showed no analytically significant levels of requested analyte.

SPIKED SAMPLE ANALYSES

Spike and duplicate spike recoveries were all within relevant control limits (75-125%).

PRECISION DATA

Precision estimates based on duplicate spike analysis were all within the acceptance criteria for duplicate analysis (+/- 20%) for all analytes. Total recoverable copper in sample 308031 was qualified as estimated due to high RPD between the sample and its duplicate (45%).

LABORATORY CONTROL SAMPLE (LCS) ANALYSES

The LCS's used for this project were in control.

Additional Quality Control Information for Wilkeson Creek Copper Analysis

SPIKE BLANKS

M1004DL3 (11.76 µg/L) and M1004DL4 (11.91 µg/L)

Laboratory spiked blanks for Dissolved Copper. True value of 10 µg/L. Used 0.025 mL 2ppm intermediate solution made from stock solution of 100 ppm (10 mL final volume).

M0348WL1 (23.38 µg/L) and M0349WL1 (22.24 µg/L)

Laboratory spiked blanks for TR copper. True value of 20 µg/L. Used 0.5 2 ppm intermediate solution made from stock solution of 100 ppm. (50 mL final volume).

STANDARD REFERENCE MATERIAL

Standard reference material SLRS-4 True value 1.81 µg/L.

M0348WL2 (2.116 µg/L), M0349WL2 (1.844 µg/L), M1004DL1 (1.672 µg/L), and M1004DL2 (1.735 µg/L)

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Appendix C - Reasonable Potential Calculations

| Parameter | Metal Criteria Translator as Decimal | | Metal Criteria Translator as Decimal | Ambient Conc. (metals as dissolved) ug/L | State Water Quality Standard | | Max Concentration at Edge of... | | Chronic Mixing Zone ug/L | LIMIT REQD? | Effluent Percentile Value | Pn | Max Effluent Conc. Measured (metals as total recoverable) ug/L | Coeff. Variation CV | s | # of Samples n | Multiplier | Acute Dil'n Factor | Chronic Dil'n Factor |
|----------------------------|--------------------------------------|---------|--------------------------------------|--|------------------------------|--------------|---------------------------------|--------------------------|--------------------------|-------------|---------------------------|-------|--|---------------------|---|----------------|------------|--------------------|----------------------|
| | Acute | Chronic | | | Acute ug/L | Chronic ug/L | Acute Mixing Zone ug/L | Chronic Mixing Zone ug/L | | | | | | | | | | | |
| copper (low flow)8-24-00 | 0.9960 | 0.9960 | 0.9960 | 0.5000 | 12.4500 | 8.5500 | 10.15 | 1.70 | NO | 0.95 | 0.688 | 36.40 | 0.23 | 0.23 | 8 | 1.30 | 5 | 39 | |
| copper (high flow)11-28-00 | 0.9960 | 0.9960 | 0.9960 | 0.4700 | 5.3400 | 3.9600 | 0.87 | 0.51 | NO | 0.95 | 0.688 | 16.35 | 0.23 | 0.23 | 8 | 1.30 | 51 | 504 | |
| copper 7-26-00 | 0.9960 | 0.9960 | 0.9960 | 0.5750 | 9.8500 | 6.9200 | 2.84 | 0.81 | NO | 0.95 | 0.688 | 34.70 | 0.23 | 0.23 | 8 | 1.30 | 20 | 187 | |
| copper 9-7-00 | 0.9960 | 0.9960 | 0.9960 | 0.4900 | 11.5500 | 7.9900 | 5.03 | 0.99 | NO | 0.95 | 0.688 | 33.40 | 0.23 | 0.23 | 8 | 1.30 | 9 | 85 | |
| copper 9-19-00 | 0.9960 | 0.9960 | 0.9960 | 0.6600 | 11.0800 | 7.6900 | 4.74 | 1.10 | NO | 0.95 | 0.688 | 35.50 | 0.23 | 0.23 | 8 | 1.30 | 11 | 102 | |
| copper 10-12-00 | 0.9960 | 0.9960 | 0.9960 | 0.5500 | 9.2600 | 6.5300 | 3.56 | 0.87 | NO | 0.95 | 0.688 | 34.20 | 0.23 | 0.23 | 8 | 1.30 | 15 | 136 | |
| copper 10-24-00 | 0.9960 | 0.9960 | 0.9960 | 0.6300 | 5.9900 | 4.4000 | 1.91 | 0.76 | NO | 0.95 | 0.688 | 27.10 | 0.23 | 0.23 | 8 | 1.30 | 27 | 261 | |
| copper 11-14-00 | 0.9960 | 0.9960 | 0.9960 | 0.4500 | 6.8000 | 4.9400 | 1.55 | 0.56 | NO | 0.95 | 0.688 | 22.50 | 0.23 | 0.23 | 8 | 1.30 | 26 | 251 | |

This spreadsheet calculates the reasonable potential to exceed state water quality standards for a small number of samples. The procedure and calculations are done per the procedure in Technical Support Document for Water Quality-based Toxics Control, U.S. EPA, March 1991 (EPA/505/2-90-001) on page 56.