Re-evaluation of Copper Impact from Wilkeson WWTP on Wilkeson Creek

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Quality Assurance Project Plan

by
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Environmental Assessment Program
Watershed Ecology Section

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Project Description

Wilkeson Creek, a tributary to the Carbon River in Pierce County (Figure 1), is on the 1998 303(d) list for exceeding aquatic life criteria for copper. The listing is based on a copper concentration of 37 µg/L measured in a composite effluent sample from Wilkeson WWTP, collected in November 1995. This concentrations was calculated to exceed the acute criterion 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 water quality criteria were actually violated.

The Town of Wilkeson has recently upgraded its treatment plant. The Washington State Department of Ecology (Ecology) Southwest Regional Office (SWRO) has requested a study to determine if the new facility has reduced copper sufficiently or if further actions are needed to protect water quality. SWRO has 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, the Environmental Assessment Program (EAP) will monitor copper concentrations in Wilkeson WWTP effluent and in Wilkeson Creek. Ancillary variables will include flow, temperature, pH, conductivity, total suspended solids, and hardness. The objectives will be 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

Sampling will be done on eight occasions, once every other week during August – 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. SWRO wants the data to represent a broad range of flow conditions and to include the months monitored by Hoyle-Dodson (1997). Sampling times for the WWTP will be varied so as not to bias the results toward certain influent loading conditions.

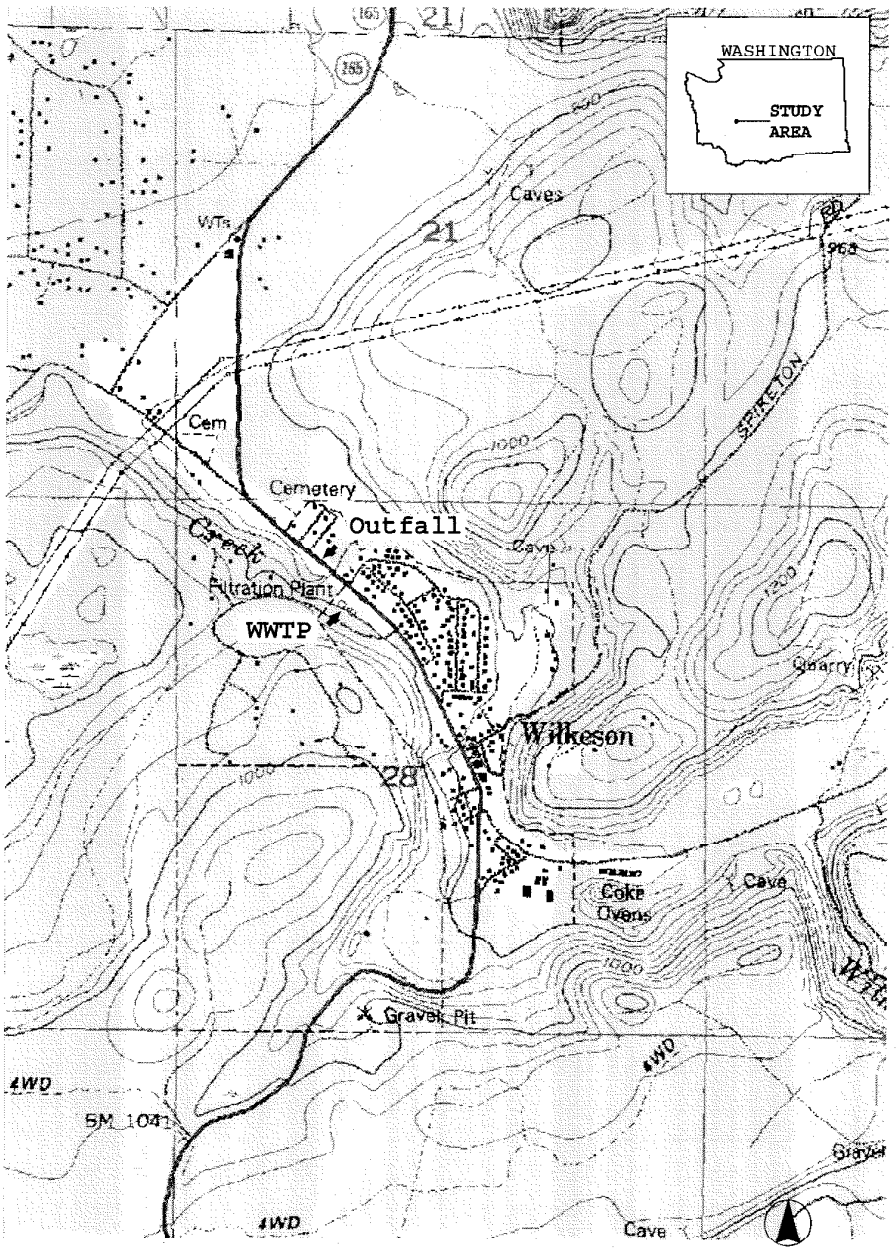

Figure 1. Study Area

Samples will be collected of the Wilkeson WWTP final effluent, Wilkeson Creek above the WWTP, and Wilkeson Creek below the WWTP. All samples will be simple grabs. The above-plant samples will be collected at a site representative of the water that mixes with the effluent. The below-plant samples will be collected beyond the edge of the

mixing zone, at a site agreed to by SWRO. Norm Glenn, EAP's mixing zone expert, will be consulted on the best location for this sample.

Total recoverable copper will be analyzed in the effluent samples. By regulation, permit limits must be expressed as total recoverable. Both dissolved and total recoverable copper will be analyzed in the downstream samples to determine what fraction of total recoverable copper is dissolved. This fraction is the metals translator needed to calculate permit limits (EPA, 1996). Analysis of the upstream samples will be limited to establishing the background level of dissolved copper.

Clean sampling techniques will be used following the guidance in EPA Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Levels* (EPA, 1995). Copper will be analyzed at the Ecology Manchester Environmental Laboratory by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Manchester's reporting limits for copper by ICP-MS are 0.05 μg/L for dissolved and 0.1 μg/L for total recoverable. Typical concentrations of dissolved copper in uncontaminated rivers and streams are 0.5 – 1 μg/L.

Table 1 shows the sample size and associated laboratory costs for the Wilkeson project.

Schedule

(exact dates to be determined)

August – November 2000.....Field Work
January 2001..... Laboratory Analyses Completed
February 2001.....Draft Report to SWRO
April 2001.....Final Report
July 2001.....Data Entered into EIM

Project Organization

Project Lead – Steve Golding, EAP (360/407-6701)
Technical Assistance – Art Johnson, EAP (360/407-6766)
Field Assistance - to be determined
Watershed Ecology Section Manager - Will Kendra (360/407-6698)
Contaminant Studies Unit Supervisor – Dale Norton (360/407-6765)
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Table 1. Number of Samples and Laboratory Cost Estimate for Evaluating Copper Impact of Wilkeson WWTP

Sample Type	Analysis	Stations or Samples	Sampling Events	Total Samples	Cost per Sample	Cost Subtotals
Field Samples[a]	Dissolved Cu	2	8	16	34	544
Field Samples[b]	Total Recov. Cu	2	8	16	68	1088
Field Samples[c]	Hardness	3	8	24	12	288
"	TSS	3	8	24	10	240
"	Conductivity	3	8	24	7	168
Field Replicates[d]	Dissolved Cu	1	3	3	34	102
"	Total Recov. Cu	1	3	3	68	204
Lab Duplicates[d]	Dissolved Cu	1	3	3	34	102
"	Total Recov. Cu	1	3	3	68	204
Field Replicates[c]	Total Recov. Cu	1	3	3	34	102
Lab Duplicates[c]	Total Recov. Cu	1	3	3	68	204
Filter Blanks	Dissolved Cu	1	2	2	34	68
Bottle Blanks	Dissolved Cu	1	2	2	34	68
Dup. Matrix Spikes[f]	Dissolved Cu	2	1	2	no charge	0
"	Total Recov. Cu	2	1	2	no charge	0
Dup. Matrix Spikes[e]	Total Recov. Cu	2	1	2	no charge	0
Std. Ref. Material	Cu	2	1	2	no charge	0
Lab Control Sample	Cu	2	1	2	no charge	0
Method Blank[g]	Dissolved Cu	1	1	1	no charge	0
Method Blank[g]	Total Recov. Cu	1	1	1	no charge	0
				+0.45 micron filters @ $21 ea =		504
				+500 mL teflon bottles @ $14 ea =		588
				+acid preservative @ $7 ea =		294
				TOTAL LAB COST =		4768

[a]Wilkeson Creek above and below WWTP

[b]Wilkeson Creek below WWTP and Wilkeson WWTP effluent

[c]Wilkeson Creek above and below WWTP and Wilkeson WWTP effluent

[d]Wilkeson Creek below WWTP

[e]Wilkeson WWTP

[f]Wilkeson Creek above WWTP

[g]to be analyzed in duplicate

Data Quality Objectives

Precision and Bias

The precision and bias routinely achieved by Manchester using the methods described in this QAPP will be satisfactory for purposes of this study. Table 2 shows recent Manchester results for copper on a certified freshwater reference material.

Table 2. Manchester Results on Standard Reference Material[a] (ug/L)

Analysis Date	Copper
April 1999	1.44
June 1999	1.41
July 1999	1.38
November 1999	1.41
certified value =	1.35

[a]SLRS-3 (River Water Reference Material for Trace Metals, Nat. Res. Council Canada)

Sources of bias from sampling procedures and sample handling will be minimized by adherence to EPA Method 1669.

Representativeness

Sampling will be conducted on eight separate occasions in an effort to obtain representative data. The time of day the effluent samples are collected will be varied to improve representativeness.

Completeness

The amount of useable data obtained will be maximized by careful planning of field work, packaging and transport of samples, and by following EPA Method 1669 sampling guidance. The laboratory will be asked to save excess sample until the data can be reviewed by the project lead.

Comparability

Sampling, quality assurance, and analytical methods are consistent with other low-levels metals work done by EAP.

Sampling Methods

Sampling methods will follow the guidance in EPA Method 1669.

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

Samples for dissolved copper will be filtered in the field through a pre-cleaned 0.45 μm Nalgene filter unit (#450-0045, type S). The filtrate will be transferred to a new pre-cleaned 0.5 liter Teflon bottle. The total recoverable and dissolved samples will be 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 will be obtained from Manchester, cleaned as described in Kammin et al. (1995), and sealed in plastic bags. Non-talc nitrile gloves will be worn by personnel filtering the samples. Filtering will be done in a glove box constructed of a PVC frame and polyethylene cover.

Flows will be measured with a Swoffer or Marsh-McBirney meter and top-setting rod. pH will be measured with an Orion model 250A. Temperature will be determined with a precision mercury thermometer.

The samples will be placed in polyethylene bags and held on ice for transport to Ecology HQ. The copper and hardness samples will be stored at 4°C at HQ and analyzed as one sample set at the end of the study; holding time is 6 months. The other samples will be transported to Manchester within one day of collection. Chain-of-custody will be maintained.

Analytical Methods

Copper will be analyzed at Manchester Laboratory by ICP-MS, following EPA Method 200.8. Total recoverable samples will be 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 will be analyzed by Standard Methods 2340B, EPA Method 120.1, and EPA Method 160.2, respectively.

Quality Control Procedures

Field QC samples will include filter blanks, bottle blanks, and field replicates, at the frequency indicated in Table 1.

Laboratory QC samples for copper will include a standard reference material (SLRS-3 or equivalent), laboratory control sample , method blank, duplicate analyses, matrix spikes, and matrix spike duplicates, as indicated in Table 1. The SRM, LCS, and method blank will be analyzed in duplicate

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

Field replicates (samples collected separately approximately 5 minutes apart) and duplicate laboratory analyses of the replicates will be used to get an estimate of the total standard deviation from sampling and analysis. The field replicates will consist of three downstream sample pairs for dissolved and total recoverable copper, and three effluent sample pairs for total recoverable copper. One sample from each of these replicate pairs will be analyzed in duplicate (split at the laboratory). These samples will be collected on three separate dates. The samples where a duplicate analysis is requested will be labeled as such.

Data Assessment Procedures and Reporting

Manchester's SOP for data reduction, review, and reporting will meet the needs of this project. Each laboratory unit assembles data packages consisting of raw data from the analyses of the samples, copies of the pertinent logbook sheets, QA/QC data, and final reports of data entered into LIMS. These data packages are subjected to a data verification and quality assurance review by another analyst familiar with the procedure. Reviewers use *Laboratory Data Validation National Functional Guidelines for Evaluating Inorganic Analyses, USEPA, July, 1988.*

The following additional information will be reported for the copper data: 1) the name, source, and certified values for SRMs and LCSs analyzed; 2) the metals concentrations measured in the SRM (in addition to percent recovery); and 3) the spiking levels used in matrix spikes.

A draft report of the study results will be provided to SWRO in February 2001. A paired comparison test will be used to determine if there is a statistically significant change from

upstream to downstream concentrations of copper. To determine if the downstream copper concentrations exceed the acute criteria, a t-test will be used to compare the difference of the sample mean from the criteria value. The project report will contain:

- a map of the study area showing sampling sites
- latitude/longitude and other location information for each sampling site
- descriptions of field and laboratory methods
- a discussion of data quality, estimates of precision and bias, and the significance of any problems encountered in the analyses
- summary tables of the metals and ancillary data
- an evaluation of significant findings with respect to upstream vs. downstream copper concentrations, exceedances of copper criteria, 303(d) listing, WWTP impact on the receiving water, and additional data interpretation as appropriate,
- recommendations for follow-up work if warranted.

A final report will be prepared after receiving review comments from SWRO and internal comments from EAP. The goal is to have the revised final report completed in April 2001. The data will be entered into Ecology's Environmental Information Management (EIM) system.

References

EPA. 1995. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Levels. EPA 821-R-95-034.

EPA. 1996. The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion. EPA 823-B-96-007.

Hoyle-Dodson, G. 1997. Puyallup Basin Treatment Plant Metals Survey. Washington State Department of Ecology. Pub. No. 97-303

Kammin, W.R., S. Cull, R. Knox, J. Ross, M. McIntosh, and D. Thompson. 1995. Labware Cleaning Protocols for the Determination of Low-level Metals by ICP-MS. American Environmental Laboratory 7(9).