A Department of Ecology Report

WASHINGTON STATE DEPARTMENT OF ECOLOGY

Results of Monitoring Copper Sulfate Application to Sylvia Lake

Introduction

During 1994, the Department of Ecology's (Ecology) Water Quality Program requested a survey of copper levels in one or more Western Washington lakes currently being treated with copper. Copper, especially in the form of copper sulfate, is widely used to control nuisance algal growth. Sylvia Lake was selected for monitoring because of concerns about copper levels in the outlet affecting fish. There was also concern about accumulation of copper in Sylvia Lake sediments due to repeated treatment.

Objectives of the Sylvia Lake survey were to: 1) Determine persistence of copper in the water column following treatment by a licensed applicator; 2) Determine concentrations of copper downstream following treatment; and 3) Measure copper concentrations in the lake sediments.

Site Description

Sylvia Lake is a small impoundment (approximately 15 acres) which serves as the centerpiece of a private residential development in Pierce County. Mean depth of the lake is estimated to be five feet, with a maximum depth of ten feet. About one-half of the shoreline is developed, while the other half appears to have been recently deforested. Hydrologic ingress appears to be mainly surface runoff and groundwater, although a small ephemeral channel was observed at the east end of the lake. The outlet is through a concrete spillway at the west end of the lake. The lake is the source of a small stream which flows for approximately one-half mile before emptying into a small embayment in Carr Inlet.

The outlet stream is used to hatch and rear several species of salmon. The Rosedale Fisheries Co-op incubates approximately 100,000 chum salmon (*Oncorhynchus keta*) eggs each year using water from the outlet stream (Conrad Dickson, Rosedale Fisheries Co-op, personal communication). Hatched fry are released to the stream during late-

by Dave Serdar
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winter or early spring and migrate seaward shortly thereafter. Washington Department of Fish & Wildlife (WDFW) has historically planted coho salmon (*O. kisutch*) fry in the stream during late-winter or early spring. In 1994, they planted 4,800 coho fry in the stream (Tom Burns, WDFW, personal communication). Coho reside in freshwater for approximately one-year before migrating seaward.

Methods

Sylvia Lake was treated with copper sulfate at mid-day on June 17, 1994. Copper sulfate was injected below the surface across the eastern two-thirds of the lake to control algae. No copper was applied within 400 ft. of the outlet. Approximately 50 lbs. (22.7 Kg)[1] of copper sulfate was used to reach a target concentration of 0.5 mg/L.[2] This would theoretically yield a copper (elemental) concentration of 62 μg/L for the entire lake, assuming complete mixing and dissolution of copper.

Sample Collection

Figure 1 shows sampling sites in Sylvia Lake and the outlet. Mark Dickson Creek was also monitored as a control site. Water column samples were collected for dissolved copper analysis at all sites just prior to treatment on June 17, 1994. Water column samples for copper and hardness were then collected from all sites at one hour, 24 hours, two days, four days, ten days, and 18 days following treatment. Measurements of pH, specific conductance, temperature, and water clarity (Secchi disk) were occasionally taken. Sediment samples for copper analysis were collected at sites SL-1, SL-3, and SL-4 prior to copper application and 18 days following treatment. Details of sample collection methods, chemical analysis, and data quality are in Appendix A.

Results and Discussion

Dissolved Copper Concentrations Before and After Treatment

Concentrations of dissolved copper and other water quality data are shown in Table 1. Changes in dissolved copper concentrations over time are illustrated in Figure 2.

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[1] Elemental copper equivalent of 12.6 lbs (5.7 Kg)

[2] Target concentration is based on portion of water column where target pest is present.

Prior to treatment, all sites except SL-1 had undetectable levels of dissolved copper (<3 μg/L) in the water column. The pre-treatment level of copper at SL-1 was 6.5 μg/L. Moderately high concentrations of copper in sediment from this site (Table 2) suggest that bottom sediments may be a continuous source of dissolved copper to the water column.

Copper concentrations at treatment sites (SL-1 and SL-2) peaked in the hours following treatment, declined substantially by 24 hours, then gradually declined during the remainder of the survey. Copper levels at all other Sylvia Lake sites lagged behind, peaking in the 24 hour post-treatment sample. One-to-two days after treatment, concentrations in the lake and upper outlet were within 40% of the predicted level of 62 μg/L, suggesting thorough mixing and dissolution of copper. After 18 days, copper concentrations in water from all Sylvia Lake sites and the upper outlet were virtually uniform at 11-13 μg/L. At the lower outlet, however, the concentration was 3.5 μg/L after only 4 days while the copper concentration at the upper outlet was 39 μg/L.

There are two possible explanations for the decline in copper concentrations between the upper and lower outlet sites. Copper may have been removed from the dissolved fraction of the water column by sorption to bed sediments, suspended sediments, or suspended colloidal material in the outlet stream. The other possibility is that one or more small tributaries to the outlet stream were causing the concentration to decrease by simple dilution. Stream discharge rates at the two sites were not measured, yet there did not appear to be a substantial difference in flow between sites.

Copper concentrations in Mark Dickson Creek remained below the 3 μg/L quantitation limit during the entire survey.

Exceedance of Water Quality Standards[3]

As expected, acute and chronic water quality standards (WQS) were exceeded at the treatment sites almost immediately after copper application. Water samples from SL-4, which was not treated, and the upper outlet did not exceed WQS until 24 hours after herbicide application. The upper outlet and the four sampling sites in Sylvia Lake remained above both acute and chronic WQS during the remainder of the survey. The WQS for copper was surpassed at the lower outlet for only one-to-two days following

[3]Ch. 173-201A WAC. The WQS for copper are based on the dissolved concentrations. WQS for copper are 7.95 μg/L for acute exposure (one-hour) and 5.64 μg/L for chronic exposure (4-day). These concentrations should not be exceeded more than once every three years on average. Copper WQS are hardness-dependent and were calculated here based on a hardness of 50 mg/L $CaCO_3$. The actual WQS may vary slightly.

copper treatment. SL-1 was the only site where the pre-treatment concentration of copper (6.5 μg/L) was at the WQS.

Potential Impacts to Fish

Many species of fish are extremely sensitive to copper in the aquatic environment. Salmonids, especially in early life stages, may be particularly sensitive, as reflected somewhat in the WQS for copper. Acute toxicity to copper is inversely related to hardness. In development of national water quality criteria, EPA lists acute toxicities from 20 tests conducted on salmonids at hardness levels between 25 and 75 mg/L (EPA, 1980). The median value (LC_{50}s or EC_{50}s) of these tests was 28 μg copper/L. Buhl and Hamilton (1990) reported 96-hour LC_{50}s of 15-32 μg copper/L to alevin and juvenile coho salmon tested in soft water (hardness of 41 mg/L), while the 24-hour toxicity to juvenile coho was as low as 23 μg/L. In a similar study using hard water (hardness of 211 mg/L), toxicity to juvenile chinook salmon (*O. tshawytscha*) was 54-58 μg copper/L (Hamilton and Buhl, 1990). Lorz and McPherson (1976) tested the effects of copper exposure on marine survival and found that out-migrating coho smolts had a reduced ability to migrate downstream and decreased seawater survival after exposure to copper at 20-30 μg/L.

Considering these data, it does not appear that copper levels in Sylvia Lake outlet following copper treatment are protective of resident or out-migrating salmonids. Dissolved copper concentrations of 20-77 μg/L likely persisted in the outlet stream for at least 24 hours on the day following treatment. In addition, copper levels of 9.5-52 μg/L and 3.5-39 μg/L persisted at an undetermined distance downstream for two and four days, respectively. Given the hardness of water in this stream (< 50 mg/L), these concentrations do not provide a sufficient margin of safety at levels where toxicity is expected to occur.

Copper Concentrations in Sediment

Table 2 shows copper concentrations in sediments before treatment and 18 days following treatment. Copper concentrations at SL-1 and SL-4 appeared to increase somewhat following treatment, but the differences are not outside the range to be expected due to normal sampling and laboratory variability.

There are currently no freshwater sediment quality criteria for Washington State. In lieu of state criteria, Ontario Provincial Guidelines (Persaud *et al.*, 1992) may be used to gauge the quality of sediments which have chemical contaminants. Although the Provincial Guidelines carry no regulatory status in Washington, the "severe effect level" for copper (110 mg/Kg) has been used by Ecology's Water Quality Program to

determine the permissibility of copper applications. The severe effect level is the concentration at which pronounced impacts to benthic organisms are expected to occur (Persaud *et al.*, 1992). Sites where sediment copper concentrations are ≥ 110 mg/Kg are generally not approved for treatment. Both the pre-treatment and post-treatment samples from SL-1 were approximately double the "severe effect level." Copper levels at SL-3 and SL-4 did not exceed, but approached the 110 mg/Kg threshold.

Conclusions

The data presented here show that concentrations of copper in Sylvia Lake water exceed state water quality standards for at least 18 days following treatment. Copper downstream of Sylvia Lake, while elevated for a short period following treatment, did not reach the high dissolved concentrations seen in the lake. While the fate of copper in the outlet stream is puzzling, dissolved concentrations which persisted for at least four days post-treatment are not sufficient to protect salmonids. As for sediments, the data suggest that copper has accumulated to levels in excess of, or approaching the maximum allowable concentration.

Recommendations

It is not advisable to continue treating Sylvia Lake with copper compounds. This is based on the potential deleterious impact to downstream salmonids as well as the accumulation of copper in lake sediments. A thorough review of potential impacts to downstream fisheries should be conducted if alternative strategies for algae or macrophyte control are to be considered.

References

Buhl, K.J. and S.J. Hamilton, 1990. Comparative Toxicity of Inorganic Contaminants Released by Placer Mining to Early Life Stages of Salmonids. Ecotoxicol. Environ. Safety 20: 325-342.

EPA, 1980. Ambient Water Quality Criteria for Copper. U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington DC. EPA 440/5-80-036.

Hamilton, S.J. and K.J. Buhl, 1990. Safety Assessment of Selected Inorganic Elements to Fry of Chinook Salmon (*Oncorhynchus tshawytscha*). Ecotoxicol. Environ. Safety 20: 307-324.

Lorz, H.W. and B.P. McPherson, 1976. Effects of Copper or Zinc in Fresh Water on the Adaptation to Sea Water and ATPase Activity, and the Effects of Copper on Migratory Disposition Of Coho Salmon (*Oncorhynchus kisutch*). J. Fish. Res. Board. Can. 33:2023-2030.

Persaud, D., R. Jaagumagi, and A. Hayton, 1992. Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario. Water Resources Branch, Ontario Ministry of Environment.

Contacts

Dave Serdar — Washington State Department of Ecology
Environmental Investigations and Laboratory Services
Toxics Investigations Section
(360) 407-6772

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Table 1. Copper and Other Water Quality Data Collected for Sylvia Lake, 17 June - 5 July, 1994.

Location	Sampling Period	Time	Diss. Copper (ug/L)	Hardness (mg/L)	pH (s.u.)	Spec. Cond. (umhos/cm)	Temp. (C)	Secchi (ft)
SL-1	Pre-Trx	1030	6.5 P	N/A	N/A	N/A	N/A	N/A
	1 Hour	1300	205	47.7	7.1	110	21.7	N/A
	24 Hours	1300	82	47.7	N/A	N/A	N/A	N/A
	2 Days	1645	59	44.7	N/A	N/A	N/A	N/A
	4 Days	1400	40	45.4	N/A	110	24.5	N/A
	10 Days	1730	18 P	46.6	7.8	110	24.6	N/A
	18 Days	1500	13 P	48.2	7.6	110	23.8	N/A
SL-2	Pre-Trx	1100	3 U	N/A	N/A	N/A	N/A	N/A
	1 Hour	1315	115	46.4	7.3	110	21.4	6
	24 Hours	1315	57	46.7	N/A	N/A	N/A	N/A
	2 Days	1700	54	46.0	N/A	N/A	N/A	N/A
	4 Days	1415	39	45.4	N/A	110	24.9	N/A
	10 Days	1800	19 P	46.5	6.9	120	23.4	7
	18 Days	1515	12 P	47.5	7.0	110	23.2	N/A
SL-3	Pre-Trx	1115	3 U	N/A	N/A	N/A	N/A	N/A
	1 Hour	1345	40	47.0	6.8	110	21.6	8
	24 Hours	1330	56	44.7	N/A	N/A	N/A	N/A
	2 Days	1715	36	51.4 J	N/A	N/A	N/A	N/A
	4 Days	1430	32	47.7	N/A	115	23.2	6.5
	10 Days	1745	16 P	55.6	7.0	135	22.9	7
	18 Days	1530	12 P	47.5	6.5	110	23.6	8
SL-4	Pre-Trx	1130	3 U	N/A	N/A	N/A	N/A	N/A
	1 Hour	1400	3 U	44.0	6.7	110	22.1	8
	24 Hours	1345	61	49.8 J	N/A	N/A	N/A	N/A
	2 Days	1730	37	51.1 J	N/A	N/A	N/A	N/A
	4 Days	1445	30 P	53.5	N/A	115	22.2	6
	10 Days	1815	18 P	45.5	6.6	115	23.7	7
	18 Days	1600	11 P	47.9	6.7	110	24.1	8
UPOUT	Pre-Trx	950	3 U	N/A	N/A	N/A	N/A	N/A
	1 Hour	1430	3 U	45.0	7.3	110	23.4	N/A
	24 Hours	1400	77	46.7	N/A	N/A	N/A	N/A
	2 Days	1745	52	44.3	N/A	N/A	N/A	N/A
	4 Days	1500	39	46.0	N/A	115	24.9	N/A
	10 Days	1830	19 P	46.5	6.8	90	23.9	N/A
	18 Days	1630	12 P	46.9	6.8	115	24.1	N/A

Table 1. (Cont'd)

Location	Sampling Period	Time	Diss. Copper (ug/L)	Hardness (mg/L)	pH (s.u.)	Spec. Cond. (umhos/cm)	Temp. (C)	Secchi (ft)
LWOUT	Pre-Trx	940	3 U	N/A	N/A	N/A	N/A	N/A
	1 Hour	1445	3 U	57.5	N/A	N/A	N/A	N/A
	24 Hours	1230	20 P	53.5	N/A	N/A	N/A	N/A
	2 Days	1600	9.5 P	56.9	N/A	N/A	N/A	N/A
	4 Days	N/A	3.5 P	59.8	N/A	150	13.3	N/A
	10 Days	1700	3 U	59.0	6.3	140	13.8	N/A
	18 Days	1430	3 U	57.6	6.6	135	15.1	N/A
MDCR	Pre-Trx	930	3 U	N/A	N/A	N/A	N/A	N/A
	1 Hour	1445	3 U	60.9 E	6.4	135	15.6	N/A
	24 Hours	1245	3 U	57.5 J	N/A	N/A	N/A	N/A
	2 Days	1615	3 U	58.9	N/A	N/A	N/A	N/A
	4 Days	N/A	3 U	58.9	6.8	140	15.4	N/A
	10 Days	1645	3 U	62.4	6.9	135	15.6	N/A
	18 Days	1430	3 U	62.0	6.6	140	15.8	N/A

N/A=Not Analyzed

U=Undetected at quantitation limits shown

P=Analyte was detected below the minimum quantitation limit

J=Result is an estimate

E=Estimated result due to interference

Table 2. Copper Concentrations in Sylvia Lake Sediments.

Location	Sampling Period	Copper Concentration (mg/Kg,dry)
SL-1	Pre-Trx	201
	18 Days	258
SL-3	Pre-Trx	101
	18 Days	80
SL-4	Pre-Trx	99
	18 Days	106

Exceeds the Ontario Provincial Guideline "Severe Effect Level"

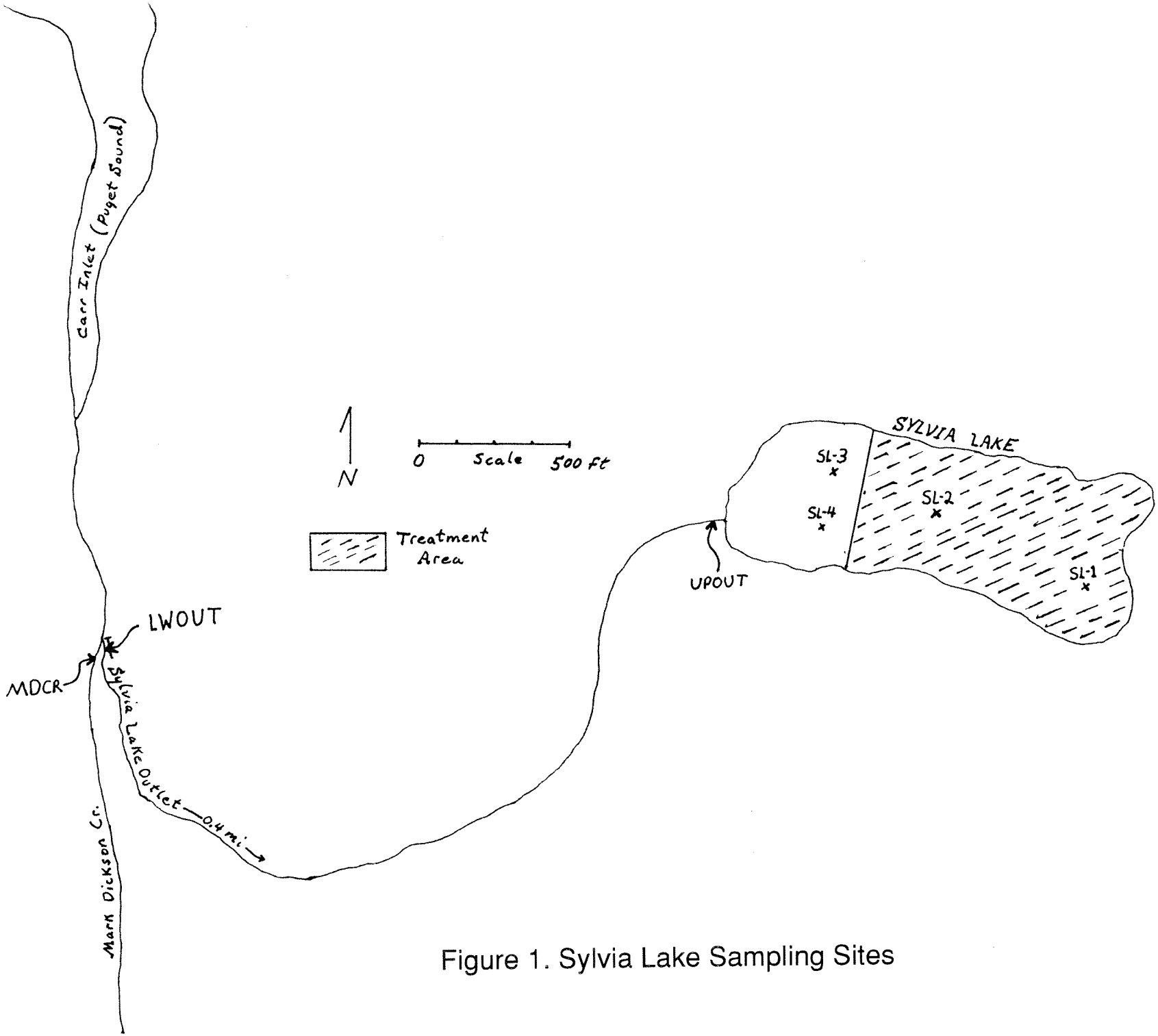

Figure 1. Sylvia Lake Sampling Sites

APPENDIX A. Sample Collection Methods, Chemical Analysis, and Data Quality

Sample Collection

Water samples at sites SL-2, SL-3, and SL-4 were collected with either a USGS depth integrating sampler or a 1.2 L Kemmer bottle. Where a Kemmer bottle was used, the sample consisted of a composite from three grabs taken near the surface, middle, and bottom portions of the water column to obtain depth integrated samples. Water samples from the other shallower sites were drawn directly into one liter cubitainers. Water samples for dissolved copper analysis were filtered (0.45 μm) in the field or laboratory and acidified (to pH $<$ 2) with nitric acid.

Sediment samples were collected with a 0.02 m^2 (petite) Ponar grab sampler constructed of stainless steel. Each sample consisted of a composite of three grabs taken from the surficial (approximately one inch) sediments. The grabs were mixed in a bucket with a sampling spoon, both of stainless steel, and placed in an eight ounce glass jar pre-cleaned for trace chemical analysis. All samples, water and sediment, were placed on ice immediately after collection.

All sampling equipment was decontaminated by scrubbing with Liquinox® detergent, followed by sequential rinses with tap water, 10% nitric acid, and deionized water. In decontaminating the Kemmer bottle, only the plastic cylinder and stainless steel shaft was rinsed with nitric acid to avoid ruining the rubber stopper ends.

Chemical Analysis and Data Quality

Water and sediment samples were analyzed at the Ecology/EPA Manchester Environmental Research Laboratory. Water samples were analyzed for dissolved copper using inductively coupled argon plasma atomic emission (ICAP; EPA Method 200.7). Hardness was measured using the titrimetric EDTA method (EPA Method 130.2). Sediment samples were prepared for total recoverable copper analysis by digesting in hot nitric acid (EPA Method 3050) and analyzed for copper by EPA Method 200.7.

Copper analysis of all samples met the EPA Contract Laboratory Program (CLP) criteria for quality assurance (see attached memo from Bill Kammin). In addition to CLP requirements, precision was also assessed by analyzing duplicate water and sediment samples submitted blind. Three pairs of duplicate water samples had a relative percent difference (RPD, difference as a percent of the mean) of 9% and one pair of duplicate sediment samples had an RPD of 5%. An equipment blank was run to assess contamination of the samples during collection, filtration, and analysis. No copper was detected in this sample at 3 μg/L.

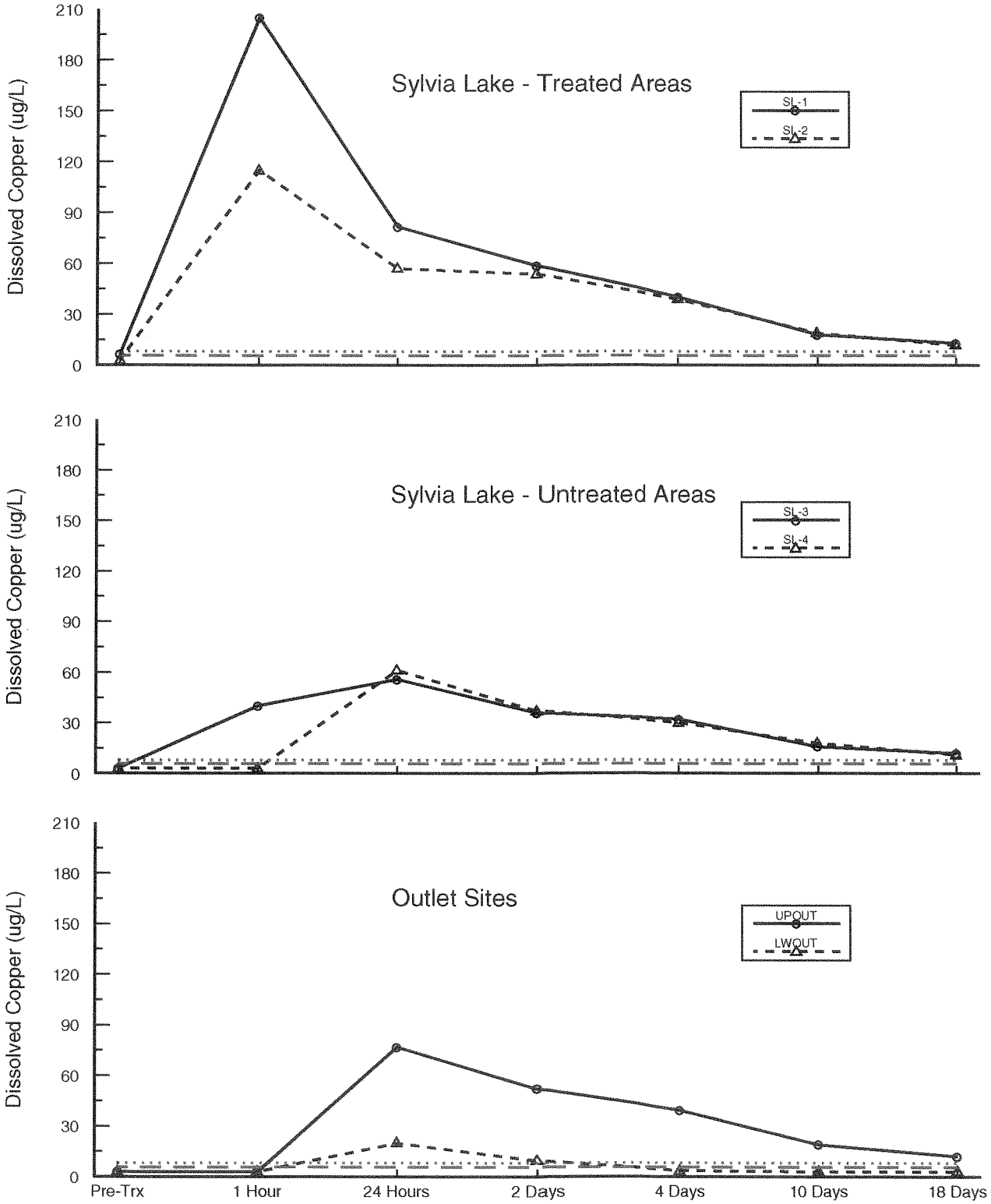

Figure 2. Dissolved Copper Concentrations at Sylvia Lake Sites

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
MANCHESTER ENVIRONMENTAL LABORATORY
7411 Beach Drive East • Port Orchard, Washington 98366-8204 • (206) 871-8860 • SCAN 871-8860

July 22, 1994

TO: Dave Serdar

FROM: Bill Kammin, Environmental_Lab_Director

SUBJECT: Metals Quality Assurance memo for the Lake Sylvia and Clear Lake Copper Project

SAMPLE INFORMATION

These samples from the Copper in Lakes project were received by the Manchester Laboratory on 6/22/94, 6/28/94, and 7/6/94 in good condition.

HOLDING TIMES

All analyses were performed within the USEPA Contract Laboratory Program (CLP) holding times for metals analysis (28 days for mercury, 180 days for all other metals).

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 analytical run. All initial and continuing calibration verification standards were within the relevant USEPA (CLP) control limits.

PROCEDURAL BLANKS

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

SPIKED SAMPLE ANALYSES

Spike and duplicate spike sample analyses were performed on this data set. All spike recoveries were within the CLP acceptance limits of +/- 25%.

PRECISION DATA

The results of the spike and duplicate spike samples were used to evaluate precision on this sample set. The Relative Percent Difference (RPD) for all analytes was within the 20% CLP acceptance window for duplicate analysis.

LABORATORY CONTROL SAMPLE (LCS) ANALYSES

LCS analyses were within the windows established for each parameter.

SUMMARY

The data generated by the analysis of these samples can be used noting the data qualifications discussed in this memo.

Please call Bill Kammin at SCAN 206-871-8801 to further discuss this project.

WRK:wrk

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
MANCHESTER ENVIRONMENTAL LABORATORY
7411 Beach Drive East • Port Orchard, Washington 98366-8204 • (206) 871-8860 • SCAN 871-8860

August 1, 1994

TO: Dave Serdar

FROM: Bill Kammin, Environmental_Lab_Director

SUBJECT: Metals Quality Assurance memo for the Sylvia Lake Sediments Project

SAMPLE INFORMATION

These samples from the Sylvia Lake Sediments project were received by the Manchester Laboratory on 7/6/94 in good condition.

HOLDING TIMES

All analyses were performed within the USEPA Contract Laboratory Program (CLP) holding times for metals analysis (28 days for mercury, 180 days for all other metals).

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 analytical run. All initial and continuing calibration verification standards were within the relevant USEPA (CLP) control limits. AA calibration gave a correlation coefficient (r) of 0.995 or greater, also meeting CLP calibration requirements.

PROCEDURAL BLANKS

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

SPIKED SAMPLE ANALYSES

Spike and duplicate spike sample analyses were performed on this data set. All spike recoveries were within the CLP acceptance limits of +/- 25%.

PRECISION DATA

The results of the spike and duplicate spike samples were used to evaluate precision on this sample set. The Relative Percent Difference (RPD) for all analytes was within the 20% CLP acceptance window for duplicate analysis.

LABORATORY CONTROL SAMPLE (LCS) ANALYSES

LCS analyses were within the windows established for each parameter.

SUMMARY

The data generated by the analysis of these samples can be used noting the data qualifications discussed in this memo.

Please call Bill Kammin at SCAN 206-871-8801 to further discuss this project.

WRK:wrk