ASSESSMENT OF COPPER IN SPECTACLE WETLAND
MOUNT WASHINGTON

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ABSTRACT

On Mt. Washington, Vancouver Island, Pyrrhotite Creek was diverted into the Spectacle Wetland as a passive remediation technique to reduce the amount of copper running into the Tsolum River. The objective of this report is to determine the concentration of loaded copper in Spectacle Wetland. We designed a systematic methodology for sampling the sediments found in the inflow, riparian, sandbars and outflow. In the Camosun College chemistry lab, the sediment underwent an Aqua Regia digestion, which removed the majority of the copper ions attached to the sediment. The samples were analyzed using an AA Spectrophotometer to determine the concentration of copper. These results underwent various statistical and visual analyses using Minitab, Ecological Methodology and Arcview GIS software. The lowest copper concentrations were found in the southeast arm of the lake, whereas higher concentrations were found throughout the rest of the lake, particularly in the outflow areas. Moderate copper concentrations were found in the inlet area, particularly in the riparian, sand bar, and stream fan areas. It can be demonstrated that high concentrations of copper are present in Spectacle Wetland. With more rigorous sampling and monitoring, for example, coring and residence time of the copper, the functionality of the wetland could be better determined.

INTRODUCTION

Environmental degradation has been occurring on Mount Washington since the copper mine was established in 1964. In an effort to reduce these effects, various passive remediation techniques have been implemented. The most recent includes a diversion of a creek into an existing wetland north of the mine. This study examines the copper concentrations found in the wetland's sediment (Walton, 2006).

In 2006, a group of Camosun College students completed a baseline study of copper in Spectacle Lake. Using systematic stratified and stratified random sampling methods, the group sampled the sediment of four major components of the wetland: sandbar, open water, riparian and outflow regions. The purpose of the study was to measure the total copper concentration in the sediment of these areas. From their study, the students concluded that all four strata exceeded schedule five of the contaminated site standards (Walton, 2006).

BACKGROUND

Mount Washington Copper mine is located 25 km northwest of Courtenay at an elevation of 1,330 m, in the Tsolum river watershed. The Tsolum River flows southeast for approximately 30 km before joining the Puntledge River, which flows into Comox Harbour and the Strait of Georgia. McKay, Pyrrhotite and Murex Creeks drain the Mount Washington mine site and are the tributaries to the Tsolum River.

Mine Site

The mine, which operated as an open-pit copper mine from 1964 to 1967, disrupted an area of 13 ha (O'Kane, 1998). After the north and south pits were abandoned in 1967, the weathering of the remaining sulphide rich minerals produced runoff with a low pH and high concentration of dissolved metals. This is known as Acid Rock Drainage (ARD). In 1988 and 1989, till was placed on the east dump. From 1990 to 1993, geotextile was placed below the south pit, and a concrete cap was placed over the west dump (Senes, 1993). In 1986, the Ministry of Environment thoroughly completed an environmental impact assessment and found that the coppers levels in the Tsolum River (70-90 µg/L) were acutely toxic to fish (Ministry of Environment, 2005). These remediation techniques were executed on the north pit to try to reduce the oxidation of the chalcopyrite and to provide suitable area for vegetation and reforestation. To mitigate the drainage, diversion ditches were created in the north pit to redirect runoff away from the east dump. After the mitigating techniques were implemented, test holes were drilled to monitor the ground water. Tests showed that oxidation was still occurring and contributing to ARD (Galbraith, 1992).

Fisheries

In the past, the Tsolum River supported large populations of various trout and salmon species. The spawning returns underwent large decreases in the 1980s to the early 1990s, and in 1982, 2.5 million pink salmon fry were released into the Tsolum River and none returned (McLean, Beggs, and Hilliar, 1996). This reduction in fish populations coincided with the operation of the open-pit mine on Mt. Washington, and in 1999, the Tsolum River was considered the most endangered river in British Columbia (Pacific Salmon Foundation, 2005). Other factors have also contributed to the decrease in returns, such as reduction of summer low flows due to irrigation usage of the river, over fishing, logging and gravel extraction. However, spawning numbers are now growing once again (BWP Consulting, 2005). Today, the water quality of the tributaries of the Tsolum River is suitable for fish, with the exception of Murex Creek (BWP Consulting, 2005). However, the mainstream of the Tsolum exposed fish to greater quantities of copper at various stages in their life cycles due to ARD. In 2001, the Tsolum River saw the best returns of pink and coho salmon in forty years, though pink salmon returns continue to be highly erratic (Phippen, 2005).

Acid Rock Drainage

Acid Rock Drainage (ARD) is a major environmental problem associated with abandoned mines and is the dissolution of chalcopyrite (copper iron sulphide) into copper and sulfuric acid. It occurs naturally in the environment but is accelerated by the disturbance caused by mining (Growitz, 2005). Most of the tailings found on Mt Washington consist of iron-copper-sulphide deposits, which is the main contributor to ARD. The sulfide minerals are oxidized not only by air and water but also by bacteria (*Acidothiocillius ferroxidans*), which are usually found in low numbers due to the lack of oxygen. The oxidation of these minerals produces sulphuric acid, which decreases the pH of the water, and increases both the concentration of dissolved metals and metal precipitation (iron hydroxide) in the streams. This acid chemically breaks down the chalcopyrite and pyrite further, dissolving copper and iron ions into the environment (Price, 1998). These dissolved metals flow through Pyrrhotite and McKay Creeks into Murex Creek and finally into the Tsolum River (Phippen, 2005). The oxidation occurring at Mount Washington is suspected to be due to precipitation and is not heavily influenced by ground water (Envipro, 2000). Copper levels may remain high enough to impact the aquatic insects, thus impacting the ability of the river to support significant numbers of coho and steelhead (Ministry of Environment, 2005). ARD is an ongoing problem at many abandoned mine sites; there is no easy way to stop air and water from being in direct contact and oxidizing the minerals.

Wetlands

Wetlands can be used as an ecologically friendly, passive-technology for filtering and treating a range of wastewater, including mine drainage. They act as a biogeochemical filter, which can treat very large volumes of water while efficiently removing low levels of contamination (Knox, 2006).

There are three parts to a wetland: the uplands, the riparian zone, and the aquatic area. As water travels through these three zones, the plants found in the wetland play an important role in purifying water. Certain plants, including water parsley, hardback, sedges, duckweeds, water lilies, bulrushes, cattails and narrow-leaved cotton grass, separate heavy metals from the water; they all accumulate heavy metals by absorbing them into their biomass (Adams 1992). Sediments play a very important role in the quality of the water by removing unwanted contaminants. When copper is dissolved, it has a 2^+ charge as an ion and has an affinity to the negatively charged soil particles, such as the fine silts, which make wetlands an ideal place to absorb copper (Coombes, 1997). “The role of organic matter in wetlands is to provide a carbon source for sulfate-reducing bacteria as well as to provide organic ligands for binding Cu and other metals” (Knox, 2006).

STUDY AREA

The wetland area this study examined is addressed by a number of names, including Spectacle Wetland and Spectacle Lake. Spectacle Wetland is located approximately 1 km north of the Mt. Washington north pit at an elevation of 1,200 m (Figure 1). In the fall of 2003, an 850 m section of Pyrrhotite Creek was re-routed through Spectacle Lake wetland as a passive remediation technique (Phippen, 2005). The east dump as well as the north pit drains into Pyrrhotite Creek, which then drains into Spectacle Lake. The main contributor to ARD on Mt Washington is precipitation, which primarily consists of the spring freshet, when the snow melts, and the watershed receives an increased amount of flow.

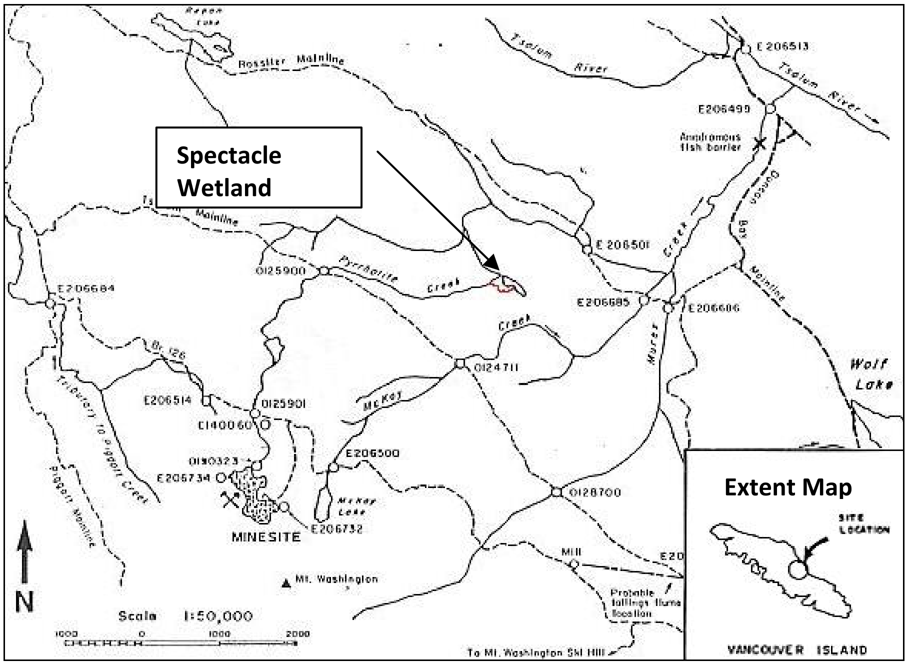

Figure 1: Mine Site and Surrounding Water Channels (Modified from Ministry of Environment, 1987)

The wetland lies on a northwest to southeast bearing and is situated in an alpine climate. The wetland hosts a number of plant species, including: Narrow Leaved Cotton Grass (*Eriophorum angustifuolium*), Yellow-green Peatmoss (*Sphagnum angustifolium*), Labrador Tea (*Ledum groenlandicum*), Skunk Cabbage (*Lysichiton americanum*), Salal (*Gaultheria shallon*), Bog Cranberry, Indian Hellebore (*Veratrum viride*), Yellow Cedar (*Chamaecyparis nootkatensis*), Sundew (*Drosera rotundifolia*), Deer Fern (*Blechnum spicant*), Salmon Berry (*Rubus spectabilis*), Devil's Club (*Oplopnax horridus*), Sitka Alder (*Alnus crispa ssp. Sinuata*) and Fir Clubmoss (*Lycopodium selago*).

METHODOLOGY

Sampling

Spectacle Lake was stratified into four sections: inflow area, outflow area, upper lake, and lower lake. Samples in these four sections were taken from the open water, riparian, sand bars, inflow, and outflow areas. The samples were distributed unevenly based upon sediment sampling results from 2006. By defining more strata, it allowed for a better representation of the lake's copper distribution (see Table 1). Transects were created in the open water area of the lake, and a riparian sampling loop was created at a maximum of two meters from the lake's edge (Figure 2).

Table 1: Number of samples in each stratum, Spectacle Lake, 2007

	Upper Lake number of samples	Inflow number of Samples	Lower Lake number of Samples	Outflow number of Samples
Riparian	7	6	6	10
Open Water	8	10	8	
In-stream		11		3
Sandbar		14		

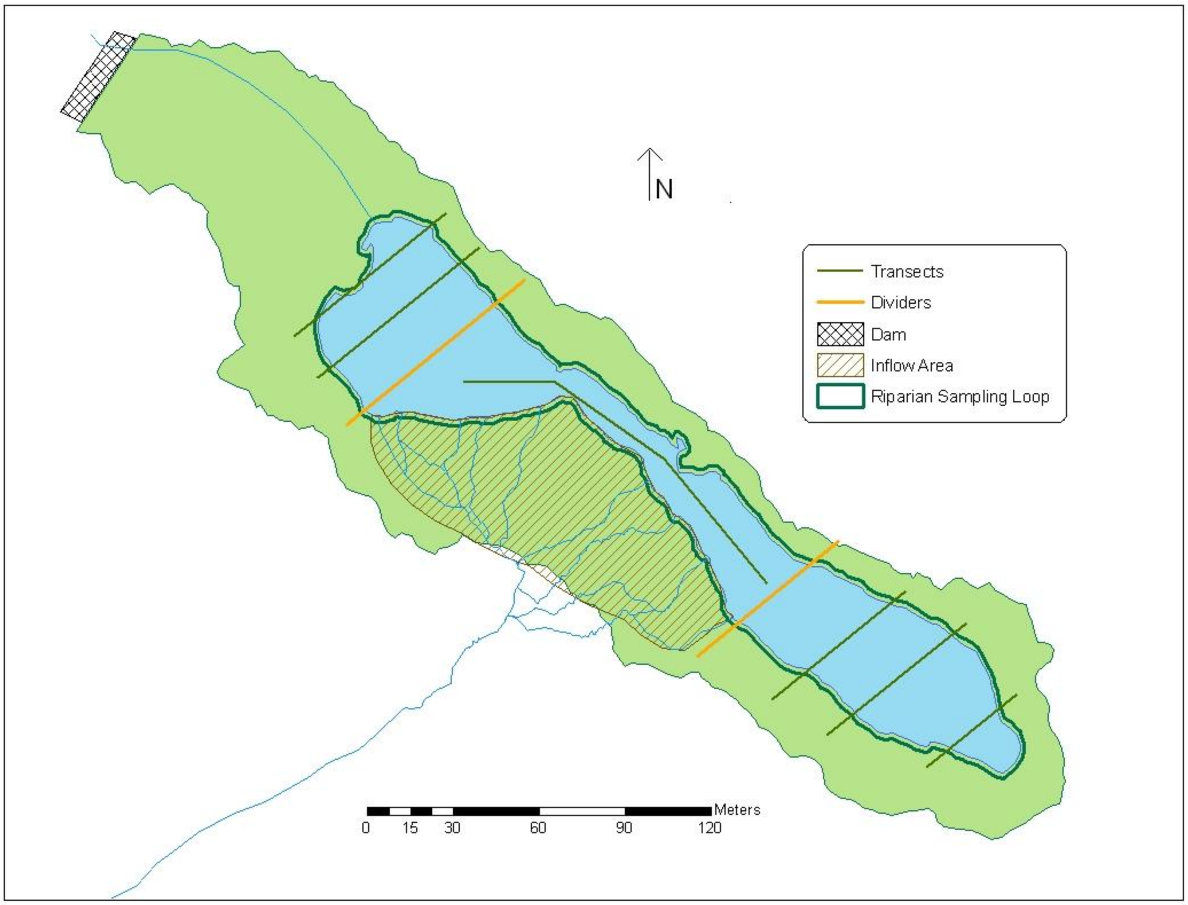

Figure 2: Sampling Design for Spectacle Wetland

<u>Analysis</u>

To remove total copper from a sample, the use of the technique known as Aqua Regia is often used. Aqua Regia is "mixture of concentrated nitric and hydrochloric acids" used to dissolve metals, including copper and gold (Camosun College Chemistry, 2006). Aqua Regia was used to extract the total copper in the sediment samples.

For the lab analysis of the samples:

- Samples were dried for 24 hours in an oven at 110 ^{o}C.
- Sub-samples were digested for two hours in an Aqua Regia solution of 50 mL de-ionized water, 7.5 mL HCl, and 2.5 mL of Nitric acid.
- The digestion was then filtered through ashless 541filter paper into 50 mL volumetric flasks.
- Copper was detected with an Atomic Absorption Spectrophotometer (AA).
- Samples that had values that exceeded 0.4 nm were diluted and re-run through the AA.
- Concentrations of digestions were determined from the standard calibration curve.
- Values for concentration of copper were converted from mg/L (wet weight) to mg/g (dry weight).

<u>Map</u>

The map was prepared using ArcView 9.2 software, and it displays the copper concentrations found in all the sampling areas (Figure 3). The graduated symbols show the range of copper, and each stratum can be differentiated by the colour. The map shows higher concentrations in the western portion of the wetland, especially the riparian and open water areas near the outflow. The inflow, which includes the stream fan, shows moderate concentrations of copper. This is assumed since the sediments are larger; they are not as proficient at binding copper in comparison to silt (Ayles, Personal Interview).

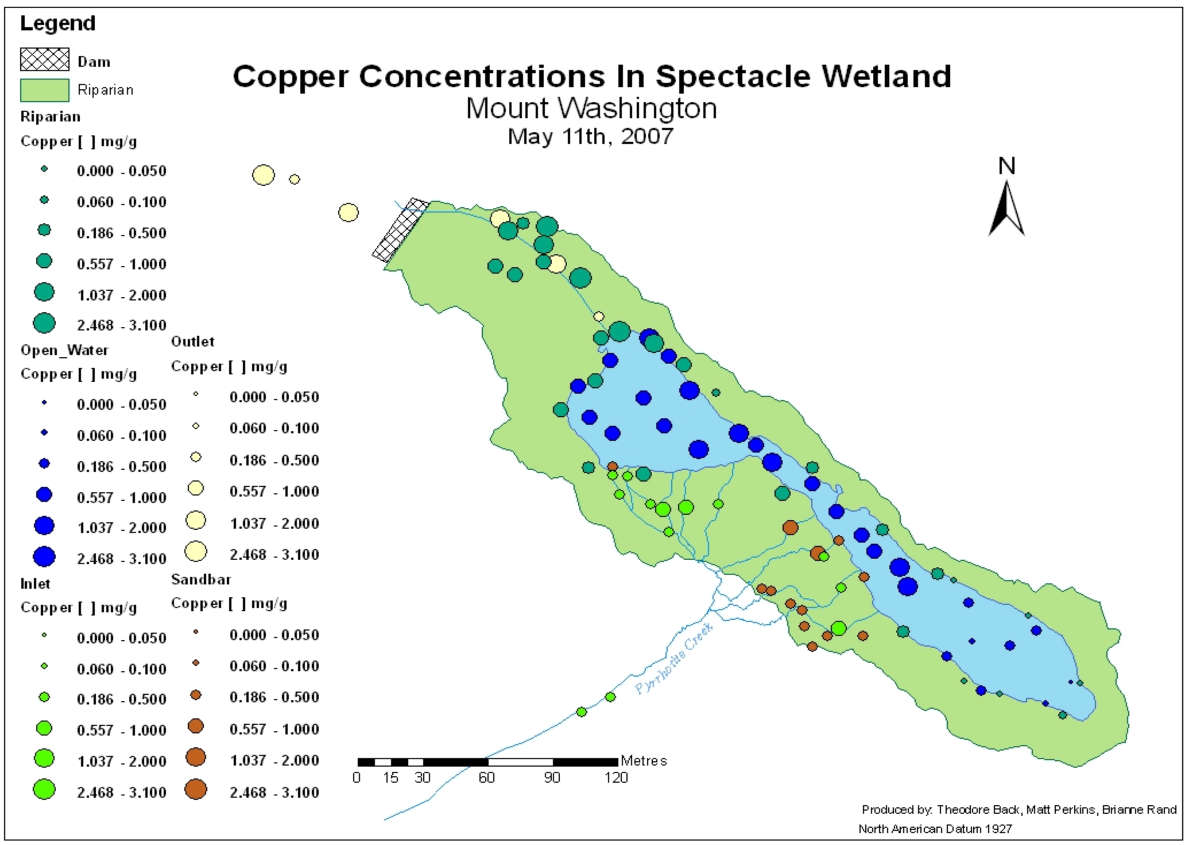

Figure 3: Copper Concentrations in Spectacle Wetland

Statistical Analysis with Square-Root Transformation of Data

The raw data that was collected was found to be non-normal. In order to proceed with parametric statistics, which have more assumptions and are therefore stronger, the dataset had to be transformed. The data was first transformed using a log transformation and was found to yield non-normal results; therefore a square-root transformation was performed and the data was deemed normal.

One-Way ANOVA

A one-way ANOVA was completed on the square-root transformed data which compares the variances and the confidence limits of each stratum. This shows how the various strata are similar and different based on the spread of the confidence limits.

The four-in-one residual plots for the output of the ANOVA statistical test done on the square-root transformations of the original copper concentrations can be seen in Figure 4. In the "Normal Probability Plot of the Residuals", normality is shown in the data set by how close the points on the graph run along the straight blue line. This is supported by the "Histogram of the Residuals" graph in the bottom left, which shows a normal distribution about the center peak. The "Residuals Versus the Fitted Values" graph in the top right exhibits a homogenous distribution by the even spread of point above and below the centerline. The "Residuals Versus the Order of the Data" in the bottom right shows the independence in the dataset by the oscillations of the points above and below the centerline.

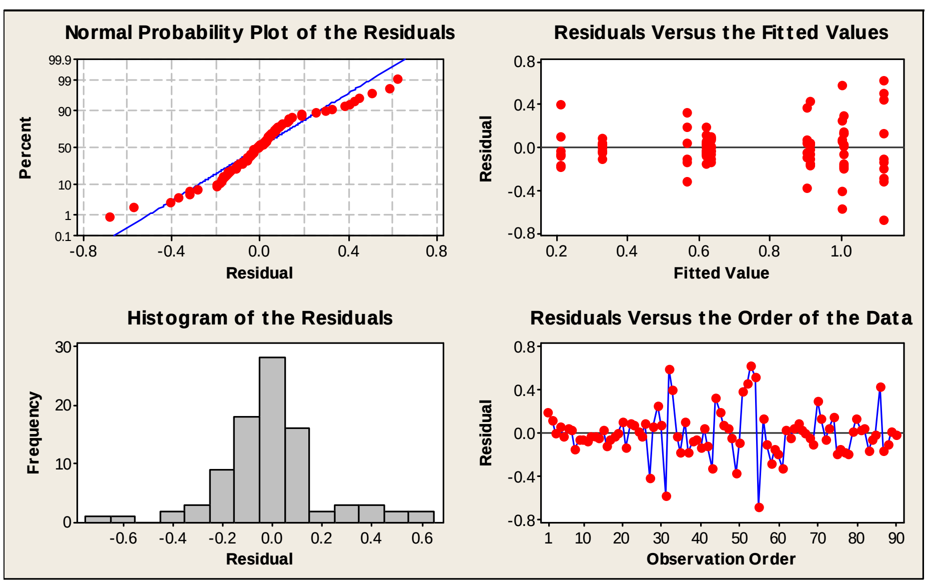

Figure 4: Residual Plots for Square-Root Transformation of Copper

The visual representation of the confidence limits (Table 2) allows for the interpretation of whether the results from each stratum are significantly different or not based on whether the parentheses visually overlap on the chart.

Table 2: One-way ANOVA

One-way ANOVA: Square Root [Cu] versus Sample

Source	DF	SS	MS	F	P
Sample	9	6.8800	0.7644	14.76	0.000
Error	78	4.0399	0.0518		
Total	87	10.9199			

S = 0.2276 R-Sq = 63.00% R-Sq(adj) = 58.74%

Table 1: Comparison of Means and Variances in Various Strata

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                               Individual 95% CIs For Mean Based on
                               Pooled StDev
Level    N    Mean   StDev   ---------+---------+---------+---------+
ULR      7  0.2117  0.2020  (----*----)
IOW     11  1.0085  0.1647                          (---*---)
IR       6  0.5645  0.2354            (----*----)
LLOW     8  0.9142  0.1902                       (---*----)
LLR      6  0.9029  0.2456                      (----*----)
OFIS     6  1.0026  0.4271                        (-----*----)
OFR     10  1.1189  0.4197                             (---*---)
SB      15  0.6202  0.0853               (---*--)
SF      11  0.6320  0.0824               (---*---)
ULOW     8  0.3285  0.0603      (---*----)
                            ---------+---------+---------+---------+
                                  0.35      0.70      1.05      1.40
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Pooled StDev = 0.2276

Individual confidence level = 99.83%

Legend

ULR-Upper Lake Riparian	IOW-Inflow Open Water	IR-Inflow Riparian
LLOW-Lower Lake Open Water	LLR-Lower Lake Riparian	SB-Sandbar
OFIS-Outfall Instream	OFR-Outfall Riparian	SF-Stream Fan
ULOW-Upper Lake Open Water	*-Mean (--)-95% Confidence Limits	

The confidence limits for the upper lake open water (ULOW) do not overlap with any other area of open water (IOW and LLOW) shown in Table 3. So it can be concluded that these strata are significantly different. In the confidence limits and variance of each of the riparian stratum (ULR, LLR, and IR), the strata are significantly different, shown by the lack of overlap. The outlet open water (OF) is not significantly different from the lower lake riparian (LLR), which is due to their proximity to each other. There is a large overlap in the inflow riparian (IR), the sand bar (SB) and stream fan (SF) strata. As the Mann-Whitney test demonstrated, the open water (OFIS, LLOW, IOW), excluding the upper lake open water, is not statistically significantly different.

CONCLUSIONS AND RECOMMENDATIONS

The lowest copper concentrations were found in the southeast arm of the lake, whereas higher concentrations were found throughout the rest of the lake, particularly in the outflow areas. Moderate copper concentrations were found in the inlet area, particularly in the riparian, sand bar, and stream fan areas. Due to a lack of consecutive annual monitoring, this study cannot determine if the passive remediation system is reducing the concentration of copper in the Tsolum River. It can be demonstrated that copper is present in Spectacle Wetland in high concentrations, and perhaps with more rigorous sampling and monitoring, the functionality of the wetland could be better determined.

In 2006, a group sampled the eastern portion of the lake for copper and found that the results were very low in concentrations, which coincides with this year's (2007) data (Walton, 2006).

Water sampling could take place throughout the wetland to get a snapshot of copper concentrations. This could demonstrate whether it is being settled out and the location of the settling. There was evidence of settling observed in the stratification seen in some sandbars and in some of the sediment in the outfall area, though this observation should be confirmed by core sampling.

Core sampling should take place in the sandbar, inflow, open water and possibly in the northern riparian area of the outflow and lower lake. This type of sampling would give a better understanding of copper that has been deposited annually. Using an ekman grab or a shovel as was done in this study, potentially mixed the sediment over a number of years.

In the case that the wetland has already reached capacity and is no longer absorbing copper, the upper lake strata (everything east of the inflow), should be exploited. This may involve another diversion to move the point of inflow east into that portion of the lake. The water moving through the inflow area could also be slowed to increase the amount of settling occurring in the inflow riparian, sandbar and stream fan areas.

The determination of residence time of water in the Spectacle Lake Wetland would also be useful. This would help to ascertain whether copper is spending enough time in the wetland for effective remediation to occur. Also, another series of sediment sampling could be done concentrating the samples above and below the wetland to show copper concentration in the upper and lower areas of the Pyrrhotite Creek.

The Spectacle Wetland has been receiving copper since 2003. With the sampling that has occurred through BWP Consulting and Camosun College, it has been determined that copper is being deposited in Spectacle Wetland due to the diversion. Due to sediment sampling, it can be concluded that the lowest copper concentrations are found in the southeast arm of the lake, whereas higher concentrations are found throughout the rest of the lake, particularly in the outflow areas. Moderate copper concentrations are found in the inlet area, particularly in the riparian, sand bar, and stream fan areas. It is possible that with more rigorous sampling and monitoring, the functionality of the wetland could be better determined.

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